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The Distribution of Cobalt and Nickel in the Di(2-ethylhexyl) Phosphoric Acid/Varsol DX3641/Tributyl Phosphate - Water System

by

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ABSTRACT

In the area of liquid-liquid extraction of metals, specifically non-precious metals like cobalt and nickel, there is virtually no binary equilibrium data available that is in a form which would be useful for design or prediction purposes. This work attempted to develop methods that could be used to represent binary equilibrium data and therefore enable one to predict binary organic phase concentrations from a knowledge of pure component equilibria and binary aqueous phase concentrations.

The system that was studied consisted of an aqueous phase comprised of cobalt and nickel sulphates and an organic phase comprised of 20 % D2EHPA, 75 % VARSOL DX3641 and 5 % Tributyl phosphate. Analogies to vapour-liquid equilibria were made in order to develop appropriate methods to predict the organic phase concentrations. Ioannou et. al.'s (52) ΔY function was used and its range of applicability was increased by modelling ΔY_A as a function of the aqueous phase mole fraction of component A (on a solvent free basis) and as a function of the aqueous phase concentration of component B.

Another method was developed in which a "pseudo" activity coefficient (called a PSEUDO GAMMA function) was used as a basis for predicting the binary organic phase equilibrium concentrations. The results showed that for both the DELTA Y and the PSEUDO GAMMA methods, while the organic phase cobalt concentrations could be predicted to within 8 % on average at 25 degrees Celsius and 4.5 % on

average at 60 degrees Celsius, the organic phase nickel concentrations could only be predicted to within 13 % at 25 degrees Celsius and 34 % at 60 degrees Celsius. The errors in the predictions for both cobalt and nickel were not randomly distributed but it was felt that this problem could largely be overcome by the development of more appropriate forms for the models used to describe the ΔY and PSEUDO GAMMA functions.

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NOMENCLATURE

Extraction Chemistry Nomenclature

ABS = the absorbance reading obtained from the Atomic Absorption Spectrophotometer.

A/O = the ratio of the volume of the aqueous phase to the volume of the organic phase.

CABS = the absorbance reading corrected for the sodium concentration.

D = the ratio of the organic phase metal concentration to the aqueous phase metal concentration at equilibrium.

DF = the dilution factor.

K = the equilibrium constant.

M = any metal ion with valence +2.

MW = the molecular weight.

P_i = the partial pressure of component i in the vapour phase.

P_i^* = the vapour pressure of pure component i

P_T = the total pressure of a two component vapour-liquid system.

PER = the % difference between the absorbance of a cobalt or nickel standard with and without sodium in it.

$pH_{0.5}$ = the equilibrium pH at which 50 % of a metal has been extracted.

$\Delta pH_{0.5}$ = the difference between the $pH_{0.5}$ values for two different metals.

Q = the ratio of organic phase metal concentration at equilibrium to the initial D2EHPA concentration.

R_1, R_2 = alkyl groups having between 8 and 10 carbon atoms.

$SF_{A,B}$ = the separation factor for component A in a binary system of A and B.

U = the sum of the squares of the differences between experimental and predicted distribution coefficients.

X = an extractant molecule without a hydrogen atom.

x_i = the aqueous phase mole fraction of component i on a solvent free basis.

X_i = the concentration of component i in the aqueous phase (gmol/l).

X'_i = the concentration of component i in the aqueous phase (g/l).

y_i = the organic phase mole fraction of component i on a solvent free basis.

Y_i = the concentration of component i in the organic phase (gmol/l).

Y'_i = the concentration of component i in the organic phase (g/l).

Y_T = the total organic phase metal concentration (gmol/l).

Y_i^* = the pure component equilibrium organic phase concentration for component i (gmol/l).

z_i = the mole fraction of component i in the liquid phase for a vapour-liquid system.

a, n, r = reaction equation coefficients.

p, q, w = reaction equation coefficients.

$[Co]_f, [Ni]_f$ = the initial metal aqueous feed concentrations (g/l)

γ = the molar activity coefficient.

γs = the PSEUDO GAMMA function.

ΔY = the DELTA Y function.

Statistical Nomenclature

Those quantities of a statistical nature that can be found in the main body of the text are explained below. The statistical quantities found in appendices are more easily explained in those sections and they are not given below.

ACT. = the actual response or independent variable.

C, E, F = parameters for Lu et. al.'s (56) model for fitting vapour liquid equilibria.

n = the number of data points that were used in the modelling procedure.

PRED. = the predicted value of the response variable.

QQ = the appropriate statistical quantity to determine if an extra parameter in an adequate linear model is required.

RESI. = the residual for the response variable.

SSR = the sum of the squares of the residuals.

$\hat{\sigma}^2$ = an estimate of the pure error variance.

$\theta, \mu, \alpha, \lambda, \beta, \phi, \eta$ = parameters for the fitted models.

Chapter I

INTRODUCTION

The use of liquid-liquid extraction for isolating metals on a relatively large scale increased dramatically during the early to mid-seventies. While the recent decline in the prices of most precious and non-precious metals has hindered the expansion of the liquid-liquid extraction field, this field is still gaining in importance.

Originally liquid-liquid extraction was used by the nuclear industry for both the separation of uranium from its ore and the separation of plutonium from uranium and its fission products in the treatment of spent reactor fuel (1). Other metals such as zirconium, halfnium and the rare earths were soon added to the list of metals that could be recovered using liquid-liquid extraction. Gradually the emphasis has been shifted towards the less valuable metals such as copper, nickel and cobalt (2). This thesis deals exclusively with the use of liquid-liquid extraction for the separation of cobalt from nickel.

During the last 15 to 20 years large strides were made in the development of extractants which show progressively greater selectivity for cobalt over nickel. The type of extractant used depends to a large degree on the nature of the leaching process used to dissolve these metals. Amine based extractants have been used to separate cobalt and nickel from primarily hydrochloric acid-leached ores (3), while carboxylic acids and chelating extractants like Kelex and LIX64N have been

used to separate cobalt and nickel from alkaline ammonium sulphate or carbonate systems (4).

The extractants which have achieved most of the attention, especially within the last 10 years, are those which can separate cobalt from nickel in sulphuric acid-leached systems. The extractants which have been successfully used and which appear to hold the most promise for future applications are phosphorous acid based extractants. These extractants can be broken down into three groups ; phosphoric, phosphonic and phosphinic acid extractants. Di(2-ethylhexyl) phosphoric acid, D2EHPA, has been the most extensively studied extractant from the above three groups. Only recently have extractants from the phosphonic and phosphinic acid groups been investigated for their potential to separate cobalt from nickel. In general, selectivity for cobalt over nickel increases as one goes from phosphoric to phosphonic to phosphinic acid.

While D2EHPA has been extensively studied, researchers have generally tended to channel their energies towards establishing the extraction chemistry of this process and/or towards showing how their particular process is better than previous ones for separating cobalt from nickel. Although these two areas are of prime importance to the better understanding and utilization of liquid-liquid extraction for the separation and purification of cobalt and nickel, they are by no means the only areas which need further study.

In most of the literature on the extraction of cobalt and/or nickel with phosphorous acid based extractants, the equilibrium data are shown as % metal extracted vs. pH, organic phase pure metal concen-

tration vs. aqueous phase pure metal concentration at constant pH, separation factor vs. pH or in some similar manner. While these methods of representing the data enable one to understand the extraction process better, they are not very practical for anyone trying to design a viable liquid-liquid extraction process. In fact there appears to be very little information in the literature which would provide a basis for the design of a liquid-liquid extraction process for the separation of non-precious metals like cobalt and nickel.

Sharma and Baird (5) touched on this subject when they determined the height of a transfer unit as a function of plate oscillation frequency for the extraction of copper using D2EHPA in a Karr reciprocating plate extraction column. Ritcey and Ashbrook (6) showed how McCabe-Thiele diagrams could be used for determining the number of theoretical stages for various types of extraction isotherms. In both cases, however, only single metal extraction was considered and therefore the data was of limited practical importance for purposes of designing a real extraction process.

To design a practical extraction process, multicomponent equilibrium data are necessary and therefore the development of methods to accurately predict multicomponent data would be extremely useful.

To address the above mentioned inadequacies in the literature, this work attempted to fulfill the following objectives;

1. Obtain both single component and binary equilibrium data for the extraction of cobalt and/or nickel in aqueous sulphate solutions at 25 and 60 degrees Celsius.

2. Express the equilibrium data in a form that would be useful for design purposes and thus establish methods that could be used to predict binary equilibrium data.

While D2EHPA is far from being the most effective extractant for the separation of cobalt from nickel in an aqueous sulphate solution, it is the cheapest. D2EHPA has been the most widely studied phosphorous acid based extractant and is the standard to which most of the other extractants have been compared. For these reasons this was the extractant chosen for this study. Since it has been widely reported that the selectivity of D2EHPA for cobalt over nickel increases with an increase in temperature, the equilibrium data were to be obtained at two different temperatures to verify the extent of this enhanced selectivity.

Chapter II

LITERATURE REVIEW

Liquid-liquid extraction as applied to the field of hydrometallurgy is a reversible technique used to concentrate and purify aqueous solutions of metals. The extraction of metals by liquid-liquid extraction is usually governed by the pH of the aqueous phase. Below a certain pH, no metal is extracted. As pH increases beyond this value, the extraction of the metal rapidly increases. Thus by controlling the aqueous phase pH, the process of liquid-liquid extraction becomes reversible.

Liquid-liquid extraction usually comprises three main steps.

1. the extraction of metal from a dilute aqueous solution into an organic phase;
2. purification of the organic phase by scrubbing with a concentrated aqueous phase;
3. recovery of the metal values from the organic phase into another aqueous phase to produce a purified concentrated aqueous solution.

Electrowinning or chemical precipitation methods are then used for the final recovery of the desired metals.

One of the most important parts of a solvent extraction process is the choice of organic phase. In industrial applications the organic phase

is usually made up of three different components; the extractant, the diluent and the phase modifier. The extractant is that compound which under specific conditions (usually pH) will preferentially extract the desired metal from the aqueous phase. Many extractants are quite viscous and have densities close to that of water. Thus, the extractants are usually dissolved in mutually soluble compounds called diluents. An effective diluent is one which improves the overall mass transfer characteristics of the organic phase and improves the separation characteristics of the two phases.

The phase modifier is used to prevent the formation of a second organic phase which may occur, especially at high metal loadings. This phase usually appears as a very thin layer of scum usually at the interface between the two main phases. The appearance of a third phase adversely affects the hydrodynamics of most contacting equipment.

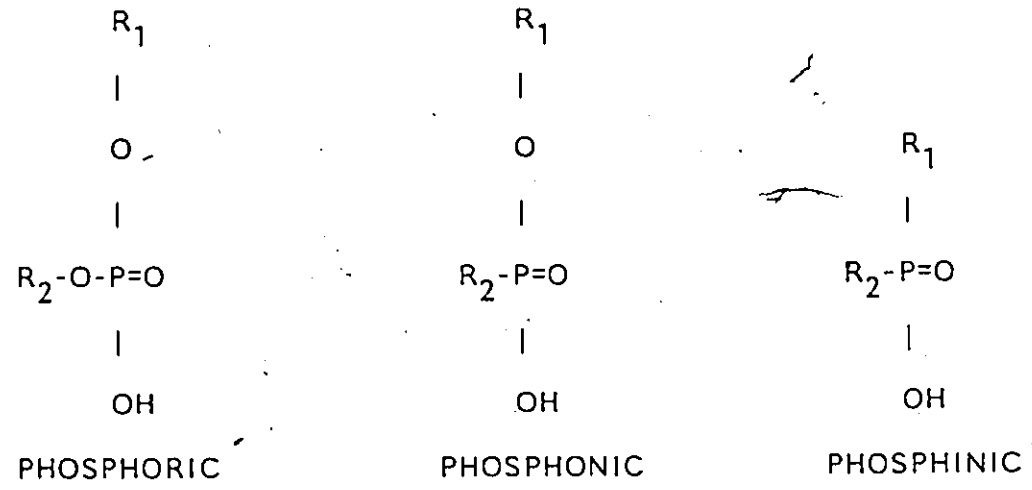
A number of important terms will now be defined to facilitate the understanding of the next few sections.

1. The distribution coefficient, D, is the ratio of the organic phase metal concentration to the aqueous phase metal concentration at equilibrium.
2. The separation factor, SF, is the ratio of the distribution factors for two co-extracted components. It is the analog of relative volatility in distillation.
3. The A/O ratio is the ratio of the volume of the aqueous phase to the volume of the organic phase.
4. The subscript "f" refers to the initial aqueous feed compositions.
5. pH refers to the equilibrium pH unless stated otherwise.

It should also be noted that all percent compositions discussed in this work are on a volumetric basis unless stated otherwise. Other pertinent definitions can be found in the Nomenclature section.

2.1 Extraction Chemistry

The three different phosphorous acid based extractants have the following chemical structures;



where R_1 and R_2 are usually alkyl groups having between 8 and 10 carbon atoms. A general equation which approximates the extraction of a metal by these acidic extractants is given below.

$$M^{2+} + 2HX \text{ <==> } 2H^{+} + MX_2 \qquad \ldots(1)$$

where M represents a metal (with valence +2), H represents a hydrogen atom and X represents the extractant without the hydrogen atom.

Equation (1) is only approximate and while there has been some work done to determine the mechanism of this process (especially with D2EHPA where $X=(C_8H_{17})_2PO_4$), the results have shown that much more work is required due to the complexity of this extraction process.

The extraction chemistry tends to be similar for each of the three groups of extractants. Thus if one studies the extraction of cobalt and nickel using a phosphoric acid one can generally expect the extraction chemistry to be stoichiometrically similar for similar phosphonic and phosphinic acids.

Madigan (7) studied the following system ;

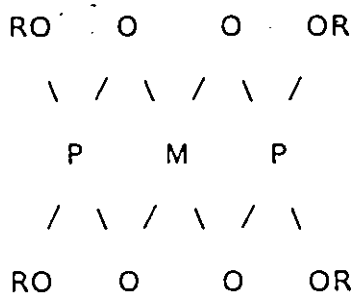
Extractant	; 0.05 M D2EHPA (sodium salt)
Diluent	; kerosene
Modifier	; 20ml/l 2-ethylhexanol
$[Co]_f$	; 1.1 to 1.3 g/l (as sulphate)
$[Ni]_f$	; 1.1 to 1.3 g/l (as sulphate)
pH	; 2.6 to 5.7
A/O	; 1.0
Temperature	; 26 degrees Celsius

He developed the following equation by assuming the extraction was carried out by equation (1).

$$\log(D) = 2(pH + \log((HX)\gamma^{0.5})) + \log(K) \qquad \ldots(2)$$

where D was the distribution coefficient, K was the equilibrium constant and γ was the molar activity coefficient for the metal ion in the aqueous phase.

From equation (2) a plot of log (D) vs. (pH + log $((HX)\gamma^{0.5})$) should yield a straight line of slope 2 and y-intercept log(K) if equation (1) was valid. Madigan found from his experimental results that for cobalt the slope was 1.55 while for nickel the slope was 1.74. He suggested that the extraction of these metals "approached" the extraction predicted by equation (1) and that the metal complex MX_2 was of the following form.



Brisk and McManamey (8) studied the following systems;

Extractant	; 0.1 to 0.5 M D2EHPA
Diluent	; kerosene
Modifier	; 10 % 2-ethylhexanol
$[Co]_f$	; 0.6 to 12 g/l (as sulphate)
$[Ni]_f$	; 1.2 to 4 g/l (as sulphate)
pH	; 2.2 to 8
A/O	; ?
Temperature	; 25 degrees Celsius

They noted that acids are dimers in non-polar solvents and hence D2EHPA should be represented by H_2X_2 instead of HX. They defined a value for Q where Q was the ratio of the organic phase metal concentration at equilibrium to the initial D2EHPA concentration. They found that the following equations described the extraction depending on the value of Q.

For Q < 0.1

$$M^{2+} + 2H_2X_2 \text{ <==> } MX_2H_2X_2 + 2H^+ \quad \ldots(3)$$

For Q > 0.1

$$M^{2+} + H_2X_2 + (MX_2)_{r-1}H_2X_2 \text{ <==> } (MX_2)_rH_2X_2 + 2H^+ \quad \ldots(4)$$

Brisk and McManamey noted that as the metal loading in the organic phase increased, the viscosity of this phase also increased. This was attributed to polymer formation as outlined by equation (4).

Sato and Nakamura (9) studied the following systems ;

Extractant	; D2EHPA
Diluent	; n-hexane
Modifier	; -
$[Co]_f$	; 60 g/l (as sulphate)
$[Ni]_f$	; 60 g/l (as sulphate)
pH	; ?
A/O	; ?
Temperature	; ?

They calculated apparent molecular weights and determined the following formulae for the metal complexes ; $CoX_2 2H_2O$ and $(NiX_2 2H_2O)_3$

Grimm and Kolarik (10) studied the following systems ;

Extractant	; 0.3 M D2EHPA
Diluent	; n-dodecane
Modifier	; Tributyl phosphate (TBP)
$[Co]_f$	; 0.006 g/l (as nitrate)
$[Ni]_f$	; 0.006 g/l (as nitrate)
pH	; 1.5 to 4.5
A/O	; ?
Temperature	; ?

They determined that the metal complexes were of the form $CoX_2 2HX$ and $NiX_2 4HX$. They also found that the higher the concentration of TBP the lower the distribution coefficient for each metal.

Barnes et. al. (11) studied the following systems ;

Extractant	; 30 % D2EHPA (sodium salt)
Diluent	; Shell Catenex II
Modifier	; -
$[Co]_f$	; 1g/l
$[Ni]_f$	; 1g/l
pH	; 5 to 5.2
A/O	; 1.0
Temperature	; 20 to 90 degrees Celsius

They showed that the distribution coefficient for nickel was virtually independent of temperature whereas the distribution coefficient for cobalt increased with an increase in temperature. This was thought to be caused by a conversion of the cobalt complex from the octahedral form at low temperatures to the tetrahedral form at higher temperatures.

$$CoX_2 2H_2O \text{ <==> } CoX_2 + 2H_2O \qquad \ldots(5)$$

The nickel complex showed no changes with an increase in temperature. It was in the octahedral form throughout the temperature range investigated.

Kolarik and Grimm (12) attempted to study the degree of polymerization of cobalt complexes in the following system;

Extractant	; D2EHPA
Diluent	; dodecane
Modifier	; -
$[Co]_f$	; 0.3 g/l (as chloride)
$[Ni]_f$	; -
pH	; ?
A/O	; 1.0
Temperature	; 23 degrees Celsius

The procedure used in Kolarik and Grimm's paper involved loading the D2EHPA/dodecane phase with cobalt and then contacting this phase

with ethylene glycol. They found that cobalt tends to form indefinitely long polymers in dodecane and that these polymers can be depolymerized by ethylene glycol as well as free D2EHPA. The polymer formation was assumed because of the large viscosity rise as the ratio of the concentration of metal in the organic phase to the concentration of free D2EHPA approached 0.5. They developed an equation for the distribution coefficient as a function of polymer formation and evaluated a quantity called U which was the sum of the squares of the differences between the experimental and predicted distribution coefficients. A species was presumed possible by a "low" value of U. They found some of the following metal polymer complexes were required for their model in order to obtain this "low" value. $(CoX_2)_{6a}$, $(CoX_2)_{20a}$ and $(CoX_2)_{120a}$ where a=1,2,...

Grimm and Kolarik (13), in another paper published in 1976, studied the D2EHPA/dodecane system with nickel. They tried to convert the octahedral nickel complex to a tetrahedral complex by heating for 30 hours at a temperature of 180 degrees Celsius but the complex remained octahedral even after a "partial decomposition of the organic part of the molecule".

It should be noted that while the authors of the previous papers did not agree exactly on the nature of the cobalt and nickel complexes, they did agree that viscosity and hence polymer formation did increase as the concentration of metal in the organic phase increased. It also seemed that the authors who determined water contents of the organic phase had complexes of the form MX_2nH_2O while the other authors tended to put the complex as MX_2nHX, where n was an appropriate

integer. It is more likely that the organic phase complex is comprised of a combination of H_2O and HX molecules. This was partially confirmed by Preston (14) who studied phosphoric, phosphonic and phosphinic acids. These were D2EHPA, PC88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) and CYANEX CNX (a phosphinic acid with unknown R groups) respectively. His systems were as follows;

Extractant	; D2EHPA, PC88A, CYANEX CNX
Diluent	; xylene
Modifier	; 25 % isodecanol (for the CNX system only)
$[Co]_f$	; 6g/l (as nitrate).
$[Ni]_f$	; 6g/l (as nitrate)
pH	; 3 to 6
A/O	; 1.0
Temperature	; 20 and 50 degrees Celsius

He found that the cobalt complex was represented by $Co(HX_2)_2$ or $CoX_2 2HX$ (using a slope analysis similar to Madigan's he found the slope to be 1.8). It should be noted that Preston found similar results for all three extractants although he published only those for PC88A in this paper.

The interesting thing about this study by Preston was the form of the nickel complex which depended on the concentration of free extractant. The equation was given by ;

$$Ni^{2+} + (2-a)H_2O + (2+a)H_2X_2 \;\langle==\rangle\; 2H^+ + Ni(HX_2)_2(H_2X_2)_a(H_2O)_{2-a} \qquad \ldots(6)$$

where a = 0, 1, 2. As the concentration of free extractant increased a increased from 0 to 2.

Komasawa et. al. (15) studied the following systems ;

Extractant	; PC88A
Diluent	; n-heptane or xylene
Modifier	; -
$[Co]_f$	; not given explicitly (nitrate)
$[Ni]_f$	; not given explicitly (nitrate)
pH	; 2.5 to 4.3 for low metal loadings
pH	; 4 to 5.7 for high metal loadings
A/O	; 1.0 or 2.0
Temperature	; 25 degrees Celsius

They used the same parameter, Q, as Brisk and McManamey to differentiate between the reaction mechanisms. For low metal concentrations they found that the extraction chemistry could be represented by these two equations;

For Q < 0.08

$$Co^{2+} + 2(HX)_2 \text{ <==> } CoX_2(HX)_2 + 2H^+ \quad \ldots(7)$$

For Q < 0.008

$$Ni^{2+} + 3(HX)_2 \text{ <==> } NiX_2 2(HX)_2 + 2H^+ \quad \ldots(8)$$

At higher metal concentrations they found that progressively larger polymers were formed. The following extraction chemistry described the system;

For Q > 0.08

$$Co^{2+} + (CoX_2)_{n-1}(HX)_2 + (HX)_2 \text{ <==> } (CoX_2)_n(HX)_2 + 2H^+ \quad ...(9)$$

For Q > 0.008

$$Ni^{2+} + (NiX_2(HX)_2)_{n-1}(HX)_2 + 2(HX)_2 \text{ <==> } (NiX_2(HX)_2)_n(HX)_2 + 2H^+ \quad ...(10)$$

As the metal concentration in the organic phase increased the value of n increased.

They also determined that at low metal loadings the sodium extraction chemistry could be represented by ;

$$Na^+ + 2(HX)_2 \text{ <==> } NaX(3/2)(HX)_2 + H^+ \quad ...(11)$$

While the above work was done with PC88A as the extractant, the authors had previously obtained similar results with D2EHPA.

In another paper by the same authors (16) they studied the interaction between cobalt and nickel in systems with similar characteristics to those mentioned above. The following equation was thought to describe the system;

$$pCo^{2+} + qNi^{2+} + (p+q+w)(HX)_2 \text{ <==> } Co_pNi_qX_{2(p+q)}w(HX)_2 + 2(p+q)H^+ \quad ...(12)$$

They determined values for p, q and w for the case where metal loading was small and where comparable amounts of the two metals were extracted as their respective monomeric species. They could not determine the values of p, q or w at conditions under which commercial operations might be run.

Danesi et. al. (17) studied the extraction of nickel and cobalt using di(2,4,4-trimethylpentyl) phosphinic acid (CYANEX 272). The systems are given below.

Extractant	; CYANEX 272
Diluent	; 0.5 F toluene ; n-dodecane
Modifier	; -
$[Co]_f$	; 0.00006g/l (as nitrate)
$[Ni]_f$	; 0.00006g/l (as nitrate)
pH	; 3.8 to 5.2
A/O	; ?
Temperature	; 25 degrees Celsius

Their slope analysis showed that a slope of 2 was obtained for both cobalt and nickel when toluene (an aromatic diluent) was used, while the slope was 1.4 for the system when n-dodecane was used as the diluent. Thus the nature of the diluent does affect the extraction chemistry. Other authors had established this a number of years earlier.

2.2 Effects of Diluent on the Extraction of Cobalt and Nickel

Bouboulis (18) studied the effect of diluent type on the Co-Ni separation with D2EHPA.

Extractant	; 15 % D2EHPA
Diluent	; mixtures of Escaid 100, Escaid 200 and

; Aromatic 150

Modifier ; 5 % TBP

$[Co]_f$; 11.9 g/l

$[Ni]_f$; 10.1 g/l

pH ; 5.8 to 7.0

A/O ; 1.0

Temperature ; 23 degrees Celsius

Bouboulis found that with TBP as the phase modifier, as the aromatic content of the organic phase increased, the ratio of cobalt to nickel in the organic phase increased. He also found that if there was no TBP present, the cobalt to nickel ratio increased dramatically and was virtually independent of the aromatic content.

Ritcey and Lucas (19) made a more comprehensive study on the diluent and modifier choice. They studied the following systems;

Extractant ; 20 % D2EHPA

Diluent ; 12 different ones

Modifier ; TBP or isodecanol

$[Co]_f$; 10 g/l (as sulphate)

$[Ni]_f$; 10 g/l (as sulphate)

pH ; 6.0

A/O ; 5.0

Temperature ; ambient ?

They found no correlation between diluent aromaticity and the ratio of cobalt to nickel in the organic phase. They also found no correlation between diluent aromaticity and separation factor. The diluents used in

Bouboulis' work were not among those used by Ritcey and Lucas. Ritcey found that both TBP and isodecanol tended to lower the distribution coefficient for rare earths. They found that the appearance of a third phase was more likely to occur when using an aliphatic diluent. The authors also noted that the organic phase containing TBP had a lower maximum metal loading but a better Co/Ni ratio when compared to the organic phase containing isodecanol. With D2EHPA as the extractant, third phase formation decreased with an increase in temperature. The authors' paper might best be summarized by saying that to choose the best diluents and phase modifiers there appears to be no better method than a trial and error procedure. However, the choice of the diluent and phase modifier does greatly affect the process since they affect both the kinetics and the equilibrium of the process.

Komasawa et. al. (20) studied the effect of diluent in the liquid-liquid extraction of cobalt and nickel using D2EHPA and PC88A. Unlike the other authors they studied single metal extraction instead of binary extraction and they concentrated on the structure of the metal complexes formed. Using non-polar hydrocarbons as diluents they discovered that "the diluent-extractant interaction was found to be relatively weak, owing to the great tendency toward self association of the extractant". The authors also found that with higher alcohols as diluents, the diluent replaced neutral extractant molecules in the octahedral nickel complex and they converted the normally tetrahedral cobalt complex to the alcohol coordinated octahedral form.

As mentioned previously, the studies undertaken with one type of phosphorous acid based extractant can generally be extended to the

other two types of extractants. The specific processes that have been used with each different extractant group will now be discussed.

2.3 Phosphoric Acid Extractants

The vast majority of studies on phosphoric acid extractants have dealt with D2EHPA due to its relatively superior extraction characteristics, availability and cost.

2.3.1 Ritcey and Ashbrook's Solvent Extraction Process

In 1968 Ritcey and Ashbrook (21) patented a process for separating cobalt from nickel in sulphate leach liquors using D2EHPA. The process is described in detail below.

2.3.1.1 Extraction

Since the aqueous feed from a leaching process contains many different materials which can adversely affect the extraction process these materials must be removed prior to the extraction. In the case of the cobalt/nickel separation the aqueous feed to the extraction column must be virtually free from all impurities such as iron, copper, arsenic, calcium and magnesium. In Ritcey and Ashbrook's process the iron and arsenic were removed by filtration and precipitation steps. The calcium and magnesium were then removed by the addition of ammonium bifluoride, while the copper was removed by solvent extraction or by cementation (22).

The extraction process was performed in a 40 ft. high pulse column. Different diameter columns were used including 2,6 and 22 inch ones. Since the published results dealt mostly with the smaller (2 inch) col-

umn the remaining parameters will be associated with this column unless stated otherwise. Ritcey used a temperature of 60 degrees Celsius because he found that as temperature increased cobalt loading increased while the amount of nickel extracted decreased. For this extraction the organic phase was continuous and the Co/Ni ratio in the feed was 0.3 to 1.5. The combined cobalt-nickel concentration in the aqueous feed was varied from 7 to 20 g/l. The ammonium salt of D2EHPA was used to avoid problems associated with low pH values. This was required because according to equation (1), if D2EHPA was used instead of the sodium or ammonium salts of D2EHPA then the hydrogen ion concentration would increase as the reaction proceeded and by Le Chatelier's principle the reverse reaction would be favoured. This was avoided by pre-equilibrating the D2EHPA using anhydrous ammonia. Sodium or ammonium hydroxide could have been used but either compound would have resulted in a two phase system in the pre-equilibration process which would have been undesirable for an industrial process. Using anhydrous ammonia resulted in only one phase for the equilibration process. Sodium and ammonium hydroxide were used, however, in small preliminary shakeout tests in which the authors assumed a reaction mechanism similar to equation (13) described the process.

$$HX + NH_4OH \overset{\nearrow}{<==>} NH_4X + H_2O \qquad \ldots(13)$$

While this mechanism for dilute systems was more clearly defined by Komasawa et. al. (see pp. 16) it appeared to be a reasonably good

approximation. The concentration of the organic phase was 20-30 % D2EHPA (NH_4), 5 % TBP to prevent third phase formation and the remainder was kerosene. Equilibrium pH was about 5.5. As the ratio of Co/Ni in the feed decreased the separation factor and the Co/Ni ratio in the loaded solvent decreased. This is very important since there are many ore types which have very low Co/Ni ratios.

2.3.1.2 Scrubbing

After passing through the extraction column the loaded solvent entered another pulse column which was used as a scrubbing column. This column was also 40 ft. high but it contained only about 27 ft. of active height. The diameter was again 2 inches. The preferred conditions were ; aqueous phase continuous, temperature at 60 degrees Celsius, A/O was varied from 0.5 to 4, pH was between 5 and 5.5. The inlet loaded organic phase contained a Co/Ni ratio of 9 while the scrubbed solvent contained a Co/Ni ratio of 40. The scrub solution contained 40 g/l of cobalt in sulphate form. As the concentration of nickel built up a bleed of the scrub recycle stream was returned to the extraction circuit.

2.3.1.3 Stripping

After passing through the scrubber, the scrubbed solvent was stripped in two mixer-settlers with 10 % sulphuric acid. This resulted in greater than 99.7 % recovery of cobalt. If nitric acid or hydrochloric acid were used as stripping solutions, concentrations of 25-30 % were required. Stripping was carried out at 60 degrees Celsius with the first stage A/O ratio being 0.143 and the second stage A/O ratio being 0.333.

One important problem was discovered with regards to the stripping process. Ritcey found that if any calcium was present in the feed it was found to be co-extracted with cobalt. The problem resulted during the stripping of the scrubbed solvent. With the two-stage mixer-settler using sulphuric acid as the stripping solution, cobalt was readily stripped, leaving the calcium on the solvent. If the calcium was stripped in a third mixer-settler, a gypsum precipitate was formed. When nitric or hydrochloric acids were used for stripping, both cobalt and calcium were stripped together. This required another treatment stage to remove the calcium from the cobalt. When using mixer-settlers with sulphuric acid as the stripping agent, the mixer-settlers would eventually have to be shut down and cleaned, whereas if a more expensive pulse column were used, a bleed stream would be required to keep the calcium buildup to a reasonable level. This bleed stream would be fed to another stage to remove the calcium.

2.3.2 Flett's "Improved Solvent Extraction Process"

Flett published a patent (23) and a paper (24) describing the patent in which he developed a process which was purported to be an improvement on Ritcey's process. Using D2EHPA as extractant, Flett found that at low organic phase cobalt concentrations and low temperatures the cobalt complex was in the octahedral form while at higher temperatures and/or higher organic phase cobalt concentrations, the complex was tetrahedral in nature. The nickel complex was always found to be in the octahedral form even at high temperatures and high nickel concentrations. Thus Flett suggested a reason as to why Ritcey found that as temperature increased the separation factor increased. However, this

was not really new, as it had already been published (see the extraction chemistry section).

Flett also said that mixer-settlers could be used instead of a pulse column for the extraction and the scrubbing sections. In his experiments, Flett used 7 or 8 extraction mixer-settlers, 3 or 4 scrubbing mixer-settlers and two stripping stages. He obtained greater than 99 % cobalt recovery and a Co/Ni ratio in the organic phase of 1000 to 1 in his final solution.

Flett also suggested that the organic phase cobalt concentration should be kept between 12 and 15 g/l to obtain the maximum separation factor, but of course this would be done anyway to minimize the extractant inventory. In Flett's paper he compared the separation factor for the separation of cobalt and nickel as a function of organic phase cobalt loading at 75 degrees Celsius. For the case where the organic phase cobalt concentration was less than 10 g/l he found the separation factor was 3.32 while it was 81.11 when the cobalt concentration was greater than 10 g/l. While this trend may have been valid, the experiment was biased in favour of the higher organic phase cobalt concentration. This can be seen from the fact that for Co < 10 g/l the A/O ratio was 0.5 and the initial Co/Ni ratio in the feed was 2 while for Co > 10 g/l the A/O ratio was 5 while the Co/Ni ratio in the feed was 4.

The ease with which one can be misled (either intentionally or unintentionally) when reading the literature can be further shown in the following example. When Flett was trying to show how much better his patent was over Ritcey's he quoted a separation factor of 4 for Ritcey's process and a value of up to 100 for his essentially identical process

(24). However, when Rickelton, Flett and West tried to show how much better phosphinic acids were over D2EHPA, they quoted a value of 14 for the Co/Ni separation factor with D2EHPA (25). Thus when reading about separation factors it is essential to know the process characteristics such as initial Co/Ni ratio, A/O ratio, temperature, diluent type, modifier type, and equilibrium pH.

The following relationships summarize Ritcey's and Flett's results for the separation of cobalt and nickel using D2EHPA.

1. As temperature increased the separation factor increased due to the enhanced selectivity of the organic phase for cobalt.
2. As the concentration of cobalt in the organic phase increased the separation factor and the viscosity increased.
3. As the concentration of free organic (D2EHPA) increased the separation factor increased but the distribution coefficients for both nickel and cobalt decreased.

2.3.3 Mass Transfer Studies

A number of authors have investigated the mass transfer rates for the extraction of metals in D2EHPA.

Brisk and McManamey (26) studied the extraction of cobalt and copper (separately) in a stirred-cell, apparatus. The extractant was D2EHPA. The diluent was kerosene and the modifier was 10 % ethylhexyl alcohol. They found that the extraction rate was controlled by both diffusion and chemical reaction rate resistances. According to these authors, the extraction reaction contributed between 30 and 75 % of the total resistance to mass transfer.

Golding et. al. (27) studied the equilibrium and mass transfer in the separation of cobalt and nickel using D2EHPA. They performed their extractions in a modified Lewis cell with an organic phase composed of 10 % D2EHPA (sodium salt), 5 % tributyl phosphate and 85 % kerosene. They found that the mass transfer rate was diffusion controlled.

Golding and Lee (28) studied the mass transfer in the extraction and separation of cobalt and nickel with 10 % D2EHPA in a pulsed sieve plate column. Mass transfer coefficients were found to be dependent on pulse amplitude and contacting region.

Golding and Saleh (29) carried out further studies on the cobalt/nickel separation in a modified Lewis cell. They found for co-extraction and scrubbing that the results suggested the mass transfer rate was diffusion controlled. However, for the stripping region they found additional resistances which could not be explained by diffusion-related processes. They postulated that this resistance could have been due to either the chemical reaction or the interface itself.

Cianetti and Danesi (30) studied mass transfer in the extraction of cobalt, nickel and zinc with D2EHPA in n-dodecane. Their experiments were performed in a forced convection, constant interfacial area stirred cell. They found that their data could be represented by 2 model types.

1. one in which the mass transfer rate was controlled by slow reversible interfacial reactions,
2. one in which the mass transfer rate was controlled by interfacial film diffusion.

They concluded that both versions of their model reduced down to a process that was diffusion controlled.

One of the advantages of liquid-liquid extraction is that it can be used to separate and purify solutions with relatively low metal concentrations. For this reason liquid-liquid extraction has been used to recover cobalt and nickel from secondary sources like scrap metals and waste sludges.

2.3.4 Separation of Cobalt and Nickel from Secondary Sources

Cook and Szmokaluk (31) described a process in use by the Pyrites company to recover cobalt from pyrite cinders and other residues like catalysts and sludges. While D2EHPA was not used to separate cobalt from nickel it was used to separate zinc, manganese, iron and copper from cobalt and nickel. The process involved the use of mixer-settlers for extraction, stripping and scrubbing. The interesting part of this process was the use of dextrose caustic in the removal of iron from the organic phase. This was required because iron was very difficult to remove using mineral acids.

The raffinate containing "purified Co/Ni" was processed using a tertiary amine solvent extraction process. It should be noted that Cook used the sodium salt of D2EHPA for this process, again to avoid pH problems. Cook's solvent extraction process removed more metal impurities than the company's previous precipitation method. The solvent extraction process produced a product with 0.35 % impurities compared to 2.22 % for the previous process. At a concentration of 10 g/l of Co, the cost of production per pound of Co using the solvent extraction process was the same as the other method but cobalt losses due to pre-

cipitation were substantially reduced using the solvent extraction process. For concentrations of Co greater than 10 g/l the cost per pound of metal for the extraction process was less than the precipitation method.

In 1978 Flett (32) reported on the extent of solvent extraction applications with regard to the recovery of cobalt and nickel from scrap and waste. He reported the closure of a company in the United Kingdom which used D2EHPA to remove zinc and copper from a nickel liquor which arose from the sulphuric acid dissolution of sludges precipitated from spent plating bath electrolytes. This company closed down some time before July 1978. The problems they encountered were indicative of the kinds of problems that many solvent purification and scrap reclaiming processes encounter. Many processes cannot tolerate organics in their process streams (like plating bath electrolytes). Thus even very small amounts of organic which get dissolved in the aqueous phase must be removed. The removal of say, D2EHPA, can be made using activated carbon but it can not be recovered from the carbon. Relatively small scale processes can't afford the loss of the costly extractant.

Flett (32) also reported on a plant which was built to treat residue from Inco's pressure carbonyl process plant. This residue treating plant was to have used D2EHPA to separate cobalt and nickel from sulphate solutions. Although the plant has been built, it had never been operated up to 1978 and no indications could be found that it had started up since then.

Ritcey and Ashbrook published another patent (33) and paper (34) in which D2EHPA was used to separate cobalt and nickel from ammonia-

cal solutions. The main difference between this process and the one used with sulphate systems was that the extraction pH in this case was about 11 instead of 5. Also, air was used to oxidize cobaltous amine sulphate to cobaltic amine sulphate which was then extracted with D2EHPA. No commercial applications could be found for this process.

There have been a number of patents issued that attempt to improve on Ritcey's original 1968 patent. Leimala (35) added a magnesium compound to the aqueous phase before extraction. This purportedly increased the separation factor between cobalt and nickel to 56. De Schepper et. al. (36) suggested using mixtures of LIX 63 and D2EHPA to effect the separation. All these improvements on Ritcey's patent have, however, been overshadowed by the use of phosphonic and phosphinic acid extractants.

2.4 Phosphonic Acid Extractants

Fujimoto et. al. (37) patented a liquid-liquid extraction process using a phosphonic acid to separate cobalt and nickel. Most of their results were obtained using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A). The authors compared the extraction of cobalt and nickel by 20 % PC88A with their extraction by 20 % D2EHPA. The extraction was carried out at 50 degrees Celsius with A/O = 1.0 and $[Co]_f = [Ni]_f = 10$ g/l. They found that PC88A was much more selective for cobalt over nickel than was D2EHPA. The authors also noted a marked increase in viscosity as the organic phase cobalt concentration increased. This was much more evident with PC88A than with D2EHPA. For PC88A they found that the temperature had little effect on the loading characteristics of cobalt and nickel.

They also carried out continuous extraction tests with two mixer-settlers for the following systems;

Extractant	; 20 % PC88A (ammonium salt)
Diluent	; kerosene
Modifier	; -
$[Co]_f$	; 13-15 g/l (as nitrate sulphate ; and chloride)
$[Ni]_f$	; 13-15 g/l (as nitrate sulphate ; and chloride)
pH	; 5.8
A/O	; 1.0
Temperature	; 50 degrees Celsius

The results indicated greater than 99 % yields for both cobalt and nickel at purities greater than 99 %. They also found that virtually 100 % of the cobalt could be stripped in 3 mixer-settlers with 1 N sulphuric acid and A/O= 0.5. Fujimoto et. al. used a scrubbing solution of 13 g/l Co in 2 mixer-settlers to reduce the nickel concentration in the loaded organic phase by a factor of 10 (A/O=0.5). The authors also found that modifiers had little effect on the extraction efficiency of PC88A. It should be noted that similar results to those above were obtained for a number of other phosphonic acids.

Motaba et. al. (38) suggested that small quantities of impurities like copper and zinc which are extracted with cobalt by PC88A could be removed by selective stripping. Their process involved keeping the stripping pH range between 1.5 and 3.5 for the removal of cobalt followed by stripping copper and zinc at a pH of less than 1.0. The preferred stripping temperature was 60 degrees Celsius.

Ogata et. al. (39) noted in their patent that there were problems of excessive viscosity when using PC88A with high metal loadings. This high viscosity resulted in problems with mixing and pumping. Their method was to control the pH in the first extraction stage to below 5.0 and preferably above 3.5. In the remaining stages the extraction was carried out at a pH between 5 and 7. This avoided the problems of excessive viscosity. A typical system was given by;

Extractant	; 20 % PC88A
Diluent	; kerosene
Modifier	; -
$[Co]_f$	; 12 g/l (coextracted as sulphate)
$[Ni]_f$	; 30 g/l (coextracted as sulphate)
pH	; as above
A/O	; 1.0
Temperature	; 60 degrees Celsius

Three extraction stages were used to effect the separation.

Ogata et. al. also performed scrubbing and stripping experiments and then recovered both cobalt and nickel by electrowinning. The metallic cobalt was 99.98 % pure while the nickel was 99.97 % pure.

Cooper and Dreisinger (40) also studied the extraction of cobalt and nickel with PC88A. They found that as the concentration of metal in the organic phase increased, the viscosity increased dramatically. The authors studied the effect of temperature on separation factor. They found that as temperature increased, the separation factor increased dramatically. They also found that the separation factor generally increased with an increase in pH but at higher temperatures the shape

of the curve became parabolic, ie. separation factor increased with pH until a maximum value was reached at which time the separation factor decreased with an increase in pH.

This increase in separation factor with temperature was found to be caused by an increase in the cobalt distribution coefficient with an increase in temperature. The nickel distribution coefficient remained relatively constant with an increase in temperature. In contrast to other authors they found that there was no evidence of an octahedral cobalt complex and hence they said that the movement of an organic complex from the octahedral to the tetrahedral form may not be the reason for an increase in separation factor with an increase in temperature for phosphorous acid based extractants like D2EHPA. Cooper and Dreisinger also found that the separation factor increased dramatically with an increase in cobalt loading. Calcium precipitation in the stripping stage was found to be a problem just as it was in Ritcey's work with D2EHPA.

Flett et. al. (41) found that for the Co/Ni-PC88A system the separation factor was between 10 and 100 times greater than the separation factor for the D2EHPA system. They also found that with an increase in aromatic content of the diluent the cobalt loading decreased but the separation factor increased. They determined that modifiers reduced the separation factor. Flett et. al. contradicted Cooper by saying that the effect of temperature, aromaticity, diluent and modifier could be correlated by the degree of formation of the tetrahedral form of the cobalt complex in the organic phase with both PC88A and D2EHPA. Cooper said that with PC88A the cobalt complex was primarily in the tetrahedral

form and therefore the increase in separation factor with an increase in temperature could not be caused by moving from an octahedral to a tetrahedral structure. While Flett et. al.'s data appear to validate their statement about aromaticity, diluent and modifier affecting the Co/Ni separation factor with PC88A, they showed no data for PC88A in which the separation factor was given as a function of temperature and % tetrahedral structure.

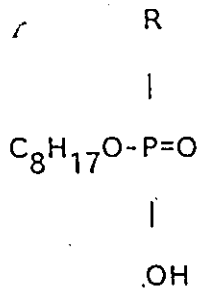
Komasawa and Otake (42) carried out a study to determine practical operating conditions for the separation of cobalt from nickel using PC88A. Their system was given by;

Extractant	; PC88A
Diluent	; n-heptane, xylene, 2-ethylhexyl alcohol
Modifier	; 10 % 2-ethylhexyl alcohol (with xylene only)
$[Co]_f$	; 3 to 6 g/l
$[Ni]_f$	; 4.5 to 15 g/l
pH	; 4.5-5.5 for extraction 3.6-5 for scrubbing
A/O	; ? for extraction 2.0 for scrubbing
Temperature	; ambient ?

They found that at high metal loadings the organic phase viscosity increased dramatically when non-polar diluents were used but it increased much more gradually if 2-ethylhexyl alcohol was used. However the alcohol had a dramatically negative effect on the cobalt/nickel separation factor. In their continuous extraction process using one mixer extraction stage and 1 scrubbing stage they obtained separation factors of 2600 when the diluent was 100 % xylene and no phase modifier was used while with a diluent system of 90 % xylene and 10 %

2-ethylhexyl alcohol, the separation factor dropped to a high of 70. Their single-stage extraction followed by single-stage scrubbing provided a final aqueous cobalt solution containing less than 0.005 % nickel when aqueous metal feed ratios were between one and two.

Chuei Biing-yi et. al. (43) showed an interesting comparison between a new phosphonic acid (called 5709), PC88A and D2EHPA. The structure of 5709 was given by the following formula where R was not divulged.



5709 was much less viscous than either of the other two extractants at 30 degrees Celsius and it was about one-half the price of PC88A (in China).

The separation factor for the separation of cobalt and nickel with 5709 from a sulphate-chloride media with an initial cobalt to nickel ratio of 1 to 300 at a temperature of 30 degrees Celsius was essentially the same as that for PC88A but for straight sulphate media and an initial cobalt to nickel ratio of 1 to 6 the separation factor with 5709 was more than three times larger than the separation factor with PC88A. In both cases the separation factor for the phosphonic acids was much higher

than the phosphoric acid separation factor. Chuei et. al. also found that calcium was extracted before cobalt with PC88A while the reverse was true with 5709. This should reduce the problems caused by calcium precipitation during stripping.

2.5 Phosphinic Acid Extractants

One of the latest developments in solvent extraction processes designed to separate cobalt from nickel involves the use of phosphinic acid extractants.

Preston (14) studied the following three extractants in xylene ; D2EHPA, PC88A and CYANEX CNX. CYANEX CNX was a phosphinic acid with R groups unknown. He studied the separation of cobalt and nickel in terms of $\Delta pH_{0.5}$. The pH at which 50 % of a metal is extracted is known as $pH_{0.5}$.

$$\Delta pH_{0.5} = (pH_{0.5})_{Ni} - (pH_{0.5})_{Co} \qquad \ldots(14)$$

For a temperature of 50 degrees Celsius, Preston found that $\Delta pH_{0.5}$ increased as the extractant moved from phosphoric to phosphonic to phosphinic acids.

Preston found that the enhanced separation of cobalt from nickel with these extractants was due to a shift in the nickel extraction curve. In other words, nickel was extracted at a higher pH for phosphinic acids than for phosphonic and phosphoric acids while cobalt was extracted at about the same pH for all three extractant types.

Preston also found that for a given extractant type the separation of Co and Ni increased as the temperature increased because of a shift in the cobalt extraction curve. In other words, for a given extractant type, as temperature increased cobalt was extracted at a lower pH while nickel extraction was at a relatively constant pH.

He discovered that for CYANEX CNX, as the concentration of free extractant increased, the Co/Ni separation factor (in terms of $\Delta pH_{0.5}$) decreased. He also found that TBP and other modifiers decreased $\Delta pH_{0.5}$. The highly aromatic xylene diluent gave higher separation factors than heptane (an aliphatic diluent).

Rickelton et. al. (25) compared the following three extractants; D2EHPA, PC88A and CYANEX 272 (di-(2,2,4-trimethylpentyl) phosphinic acid). They used the following systems for each of the above extractants.

Extractant	; 0.1 M D2EHPA, 0.1 M PC88A and
	; 0.1 M CYANEX 272
Diluent	; MSB 210
Modifier	; -
$[Co]_f$	; 1.5 g/l
$[Ni]_f$	; 1.5 g/l
pH	; 2 to 6.2
A/O	; 1.0
Temperature	; 25 degrees Celsius

The authors showed that the separation factor increased dramatically in going from D2EHPA to PC88A to CYANEX 272.

These same authors reported on another experiment comparing D2EHPA and CYANEX 272. This system was given by;

Extractant	; 0.4 M D2EHPA , 0.4 M CYANEX 272
Diluent	; Aromatic 100
Modifier	; -
$[Co]_f$	; 2 g/l (coextracted as sulphate)
$[Ni]_f$	; 100 g/l (coextracted as sulphate)
pH	; 2 to 6.2
A/O	; 1.0
Temperature	; 50 degrees Celsius

CYANEX 272 was clearly superior in separating cobalt and nickel but it still extracted some nickel into the organic phase.

Rickelton et. al. (25) also developed a continuous extraction scrubbing system that they used to obtain a scrubbed solvent with a Co/Ni ratio greater than 1000 and a raffinate containing less than 10 ug/l of cobalt. The system characteristics are given below.

Extractant	; 20 % CYANEX 272 (ammonium salt)
Diluent	; 70 % MSB 210
Modifier	; 10 % p-nonylphenol
$[Co]_f$	; 2 g/l (coextracted as sulphate)
$[Ni]_f$	; 99 g/l (coextracted as sulphate)
pH	; 6
A/O	; extraction 2.0 scrubbing 0.031
Temperature	; 50 degrees Celsius

Both extraction and scrubbing were carried out in mixer-settlers with a 3.5 minute residence time. The scrub solution contained 40 g/l cobalt as sulphate. The authors did not show any stripping results.

In another paper by these same authors (44) it was found that CYANEX 272 extracted cobalt in preference to calcium. They said that "this can minimize or eliminate the solvent losses which are associated with extraction and the subsequent precipitation of gypsum cruds". The authors give the following pH functionalities for D2EHPA, PC88A and CYANEX 272;

D2EHPA	Zn > Cu > Co > Ni > Mg > Ca	(Ritcey)
D2EHPA	Zn > Ca > Cu > Mg > Co > Ni	(Flett)
PC88A	Zn > Cu > Ca > Co > Mg > Ni	(Flett)
CYANEX 272	Zn > Cu > Co > Mg > Ca > Ni	(Flett)

Also included is Ritcey's functionality for D2EHPA. If Ritcey's relationship is correct, then CYANEX 272 may not be any better than D2EHPA for having less calcium precipitation. However, if Flett's relationship for D2EHPA is correct, then CYANEX 272 may in fact be more effective in reducing calcium precipitation. This is another example of the many contradictions that exist in the literature in this field.

Most of the above work on phosphinic acid extractants was based on Rickelton et. al.'s patent (45) for separating cobalt and nickel by solvent extraction using phosphinic acid extractants.

Rickelton et. al. studied a number of phosphinic acid extractants, all of which appeared to sucessfully separate cobalt and nickel. For the system shown below he obtained 100 % cobalt extraction and only 3 %

nickel extraction at a pH of 5.52. This, of course, resulted in a separation factor of infinity.

Extractant	; CYANEX 272
Diluent	; Solvesso 100
Modifier	; 5 % isodecanol
$[Co]_f$	; 1.97 g/l (coextracted as sulphate)
$[Ni]_f$	; 93.6 g/l (coextracted as sulphate)
pH	; 2.8 to 5.6
A/O	; 1.0
Temperature	; 50 degrees Celsius

They mentioned one stripping test where a loaded organic with 1.56 g/l cobalt and 4.92 g/l nickel was stripped with 3 % sulphuric acid at 50 degrees Celsius and A/O was 1.0. Over 92 % of the nickel was stripped but only 25.6 % of the cobalt was stripped. Another example they gave involved a highly loaded organic phase (both cobalt and nickel) which was stripped with 5 % sulphuric acid at 50 degrees Celsius with A/O = 0.5. They obtained 100 % cobalt stripping with supposedly only one contact. This seems hard to understand when compared to the previous result.

2.6 Industrial Applications for Primary Sources

Research into the separation of cobalt and nickel by phosphorous acid based extractants has progressed from studing phosphoric, phosphonic and now phosphinic acid extractants. At the present time there are not many known commercial processes using these extractants. Flett (46)

reported that D2EHPA was used by Matthey Rustenburg Refiners in South Africa. They produced about 2500 t/yr of cobalt sulphate. The economics of this process may be improved by using PC88A or CYANEX 272 since the ore they processed had a low Co/Ni ratio and they had to concentrate a solution of 250 g/l Ni and 2-4 g/l Co to one of 30 g/l Co and 15g/l Ni before successful extraction with D2EHPA could be carried out (25).

Flett also reported that PC88A had replaced D2EHPA as the extractant in the Japanese Nippon Mining Company. They used centrifuges for their extraction process and produced 3600 t/yr of nickel and 1200 t/yr of cobalt using electrowinning of the metals from sulphate electrolytes (46).

Commercial plants using CYANEX 272 may soon be realized due to the superior extraction capabilities of this phosphinic acid extractant.

Since this thesis is primarily concerned with the representation of data, a brief review of the literature dealing with the modelling of liquid-liquid extraction equilibrium data will now be given.

2.7 Modelling Equilibrium Data

There are three main types of models which can be used to represent data in general and more specifically, equilibrium data. These include ;

1. mechanistic models which attempt to model the data on the basis of the known chemistry of the extraction;
2. semi-empirical models which make use of analogies between vapour-liquid equilibrium and gas adsorption;

3. totally empirical models which are not based on any theory. They involve generalized mathematical expressions for eg., polynomials.

While mechanistic-based models are perhaps the most desirable due to the fact that model extrapolations have some theoretical basis, they have a number of limitations. These models are only as good as the proposed reaction equations which describe the system. In the case of the cobalt/nickel separation it can be seen from the extraction chemistry section that the exact mechanism for the extraction process is generally not known. In fact, it depends not only on the extractant but also on the diluent and phase modifier which researchers have failed to take into account in any of their proposed mechanisms. It should also be mentioned that to make the models thermodynamically consistent one would be required to obtain activity coefficient data. A number of attempts have been made to approximate the activity data (7,8,47), but because of the system complexity it appears that these approximations are only valid for extremely dilute systems which are not of practical importance.

Since liquid-liquid extraction isotherms have similar shapes to adsorption isotherms the model forms which describe adsorption isotherms have been used to describe liquid-liquid extraction isotherms (48,49). Two of the most popular equations are the Langmuir and Freundlich isotherms.

$$Y_A = \theta_1\theta_2 X_A / (1+\theta_2 X_A) \qquad \text{LANGMUIR}$$

$$Y_A = \theta_3 X_A^{\theta_4} \qquad \text{FREUNDLICH}$$

In the adsorption field, the Langmuir isotherm describes the adsorption of single solutes on completely homogeneous surfaces. It is applicable to systems with negligible interaction between adsorbed molecules. θ_1 represents the asymptotic maximum solid-phase concentration and θ_2 is the equilibrium constant (50).

The Freundlich isotherm is an empirical equation which has been applied to the adsorption of solutes from dilute solutions (51).

Analogies to vapour-liquid equilibrium have also been made. Ioannou et. al. (52) studied the extraction of lanthanides by D2EHPA. An analogy to the well known combination of Dalton's law of partial pressures and Raoult's law for ideal solutions was used for a binary system containing components A and B. For the vapour-liquid system the following equation is valid.

$$P_T = p_A + p_B = P_A^* z_A + P_B^* z_B \qquad \ldots(15)$$

where P_T is the total pressure, p_i is the partial pressure of component i in the vapour phase, P_i^* is the vapour pressure of pure component i and z_i is the mole fraction of component i in the liquid.

Ioannou proposed the following analogies for liquid-liquid systems.

Y_T, the total organic phase metal concentration, corresponded to P_T

Y_i^*, the pure component equilibrium organic phase concentration of component i, corresponded to P_i^*

x_i, the aqueous phase mole fraction of component i based on only A and B (ie., solvent free), corresponded to z_i

Since equation (15) is only applicable to ideal solutions Ioannou et. al. added terms in their analogous equation to take into account the non-ideality of their system. Their equation was as follows;

$$Y_T = Y_A + Y_B = (Y_A^* x_A + \Delta Y_A) + (Y_B^* x_B + \Delta Y_B) \qquad \ldots(16)$$

where ΔY_A and ΔY_B were terms to take into account deviations from ideality.

Using this approach, the authors were able to predict organic phase concentrations from a knowledge of aqueous phase compositions, the pure component isotherms and the separation factor. In fact the authors went further than binary systems and applied their method to ternary systems. Their results and method will be discussed in much more detail in the results and discussion section.

Chapter III

EXPERIMENTAL PROCEDURE

Equilibrium data for the extraction of cobalt and/or nickel from aqueous sulphate solutions with D2EHPA were obtained by conducting simple shakeout experiments. The organic phase was comprised of 20 % D2EHPA, 75 % VARSOL DX3641 and 5 % tributyl phosphate. This mixture provided good mass transfer characteristics for attaining equilibrium and for minimizing settling times. It also provided reasonably high metal loadings per unit weight of extractant. The phase modifier was effective at stopping third phase formation. The phase modifier was kept at only 5 % due to its inhibiting effect on the cobalt/nickel separation .

The organic phase was pre-equilibrated with an aqueous solution containing 100 g/l of sodium hydroxide and 50 g/l of ammonium sulphate. The high concentration of ammonium sulphate was required to keep the aqueous phase ionic strength high enough so that phase disengagement was complete. Approximately 800 ml of the organic phase and 200 ml of the pre-equilibration aqueous phase were shaken up in a 2000 ml volumetric flask for about 5 minutes. If the sodium was extracted according to equation (13) and if the reaction went to completion the amount of sodium hydroxide used in this pre-equilibration would result in 100 % saturation of the organic phase. The actual saturation (assuming equation (13) to be correct) was approximately 75 %.

After shaking, the phases were allowed to settle overnight and were then separated in a separatory funnel. 50 ml samples of the now equilibrated organic phase and 50 ml samples of metal-containing aqueous solutions were then added to 200 ml volumetric flasks. The aqueous solutions consisted of 20 g/l of ammonium sulphate, varying amounts of cobalt and nickel sulphate and their pH was adjusted to a pH of 4±0.02 . When this initial pH was used, all equilibrium pH values were between 5.3 and 6.4. At these pH values, both cobalt and nickel loadings were at or near their maximum loadings ((6), pp.107). In other words at these pH values the pH had a negligible effect on the equilibrium concentrations. Analytical reagent grades were used for all runs. Sample chemical specifications can be found in Appendix G. The volumetric flasks containing the aqueous and organic phases were then shaken manually for 3 minutes and placed in a constant temperature shaker-bath and shaken at a speed of about 1.8 cycles/sec. for one hour. It was reported (23) that equilibrium could be achieved with this system in about 2 minutes. Therefore, after 1 hour of constant shaking, the system was assumed to be at equilibrium. This was checked by shaking for longer periods of time but no significant differences in equilibrium concentrations were found. The shaker was then turned off and the phases were allowed to separate overnight. The temperature was kept constant at either 25±0.5 or 60±0.5 degrees Celsius. The next day aqueous phase samples of approximately 20 ml were removed from each flask still in the constant temperature bath. The samples were removed using a 20 ml hypodermic syringe. A portion of each aqueous phase sample was diluted to an appropriate concentration (1-6 ppm for

cobalt and nickel) and were analyzed using a Jarrel Ash Atomic Absorption Spectrophotometer (AAS) (see Appendix A for an explanation of the experimental equipment used in these experiments). The remaining portion of the aqueous phase was then used to determine the equilibrium pH.

Organic phase samples for some runs were also taken. Organic phase samples were stripped with 4 washings of 5 % sulphuric acid. The stripping was done at room temperature in separatory funnels with an A/O ratio of 1. The resulting stripped aqueous solution was then diluted to an appropriate concentration and then analyzed on the AAS.

There were a number of problems encountered in the analysis of the samples. It was found that the sodium from the pre-equilibrated organic phase, which ended up in the aqueous phase after the extraction, interfered with the absorbance of both cobalt and nickel. This resulted in an apparent enhancement of the absorbances of cobalt and nickel by at most 11 %. Almost all of the data were taken in the range where the enhanced absorbance was between 2 and 5 % for cobalt and 4 to 7 % for nickel. It should be noted that the presence of cobalt and nickel did not noticeably affect the absorbance of each other at the concentrations used in this experiment.

Other hydroxides like potassium or ammonium could have been used but there were problems associated with using these as well. Potassium hydroxide presented enhanced absorbance readings similar to those of sodium hydroxide. Ammonium hydroxide is quite volatile and therefore after the ammonium hydroxide solution is opened a number of times, the exact concentration would not be accurately known and hence the

degree of saturation of the organic phase would not be constant or known. It was shown (53) that even for small differences in the level of saturation of D2EHPA with ammonium hydroxide significant differences in the equilibrium concentrations could be expected. Thus keeping the saturation level constant was of paramount importance.

The proper equipment for determining the ammonium concentration in either phase was not readily available while the sodium concentrations could be determined using the AAS. The use of sodium hydroxide was therefore found to be necessary and an appropriate correction factor was applied to all aqueous phase absorbance readings to correct for the presence of sodium. A detailed explanation of this correction factor can be found in Appendix D.

Problems were also encountered in the organic phase analysis. For low total metal concentrations (< 7.5 g/l) problems were encountered in confirming mass balances when both organic and aqueous phases were analyzed. Differences of as much as 15 % were found. All these differences were positive. The total metal concentration as determined with the AAS by analyzing both aqueous and organic phases was always greater than the total feed metal concentration determined by weighing the cobalt and nickel sulphate crystals. At higher concentrations (> 7.5 g/l) mass balances were confirmed to within 5 %. The reason there appeared to be problems with the organic phase analysis was that for total metal concentrations below 7.5 g/l the organic phase metal concentration determined by the AAS was, by itself, greater than the total feed metal concentration! If there was a discrepancy one would have expected that it would have been caused by the fact that not all of the

metal would have been stripped from the organic phase. If this were the case, mass balances less than that of the feed metal concentration would have been expected. Attempts were made to determine if the pH or trace levels of the organic phase were interfering with the metal absorbance but, at the levels tested, neither of these factors appeared to have had an appreciable effect on the metal absorbance. For this reason the aqueous phase analysis was used and after the sodium correction factor was applied the total feed metal concentration was used to determine the corresponding organic phase concentration.

Chapter IV

RESULTS AND DISCUSSION

4.1 Brief Statistical Background

When any type of model is developed to represent or to fit experimental data it is important to know if the model is a reasonable representation of the data. It is also important to know how precise the parameter estimates and any model predictions are.

Ideally, one would like a model that shows no signs of inadequacies, that has unbiased parameter estimates and that has parameter estimates that are as precise as possible. One would also like the random errors associated with the model to be normally distributed so that quantitative statistical tests could be performed which would provide more information about the model. If a model does not have all of these desired properties the conclusions that can be drawn from it and the confidence that can be placed on any model predictions will be limited. However, as long as these model limitations are recognized and taken into account when utilizing a model the results should not be misinterpreted.

The modelling done in this thesis used a least squares analysis as the curve fitting criterion. The least squares criterion involves minimizing the sum of the squares of the residuals. A residual is defined as the difference between the actual response (or dependent) variable and the predicted response variable.

For linear models, and asymptotically for nonlinear models, least squares estimates are unbiased and of all linear unbiased estimates they have the minimum variance. If the additional assumption is made that the random error term is normally distributed then the parameter estimates will be normally distributed and various quantitative statistical tests can be performed to rule out any model inadequacies.

There are a number of assumptions inherent in least squares analysis.

1. The model is correct, or in other words, the expected value of the random errors is zero.
2. The value of the independent or operating variables are known exactly or at least much more accurately than the response variables.
3. The variance of the random error term is constant across the observations.
4. The random errors are uncorrelated across observations.

Thus, when analyzing any linear least squares regression problem these assumptions must be valid for the parameter estimates to be unbiased and have minimum variance. For models that are nonlinear in the parameters a least squares analysis will not necessarily produce estimates that are unbiased and these estimates will not necessarily have minimum variance. These properties are only asymptotically approached as the number of data points increase.

In liquid-liquid as well as vapour-liquid equilibrium experiments the usual method of obtaining equilibrium concentrations involves putting a known quantity of material in some vessel and after equilibrium has

been achieved measuring the concentrations of the material in both phases. The resulting concentrations corresponding to each phase are usually plotted against each other. Any modelling of this data using a least squares criterion will result in assumption 2 being broken because the error in the "independent" variable will be comparable to the error in the "dependent" variable. A method which takes these errors in both variables into account has received increasing attention in the last few years. Reilly and Patino-Leal (54) suggest that the use of this method, called Error-In-Variables (or EVM), is a more realistic approach for modelling in these situations and gives a more accurate representation for parameter confidence regions. Implementing EVM was beyond the scope of this thesis so that ordinary least squares was used, with the understanding that assumption number 2 was violated.

Another problem which arises due to the nature of equilibrium experiments is that any replicate runs which are performed replicate the initial conditions prior to equilibrium and not the conditions under which the modelling is performed. For this reason it is difficult to obtain an accurate estimate of the pure error variance associated with the "dependent" variable since this depends on the variance of the "independent" variable.

In order to perform quantitative lack of fit tests to check models for apparent inadequacies an estimate of the pure error variance is required. Since this was not available for any of the equilibrium concentrations quantitative lack of fit tests were not performed. The ratio of the sum of squares of residuals (SSR) divided by the difference between the number of data points (n) and the number of parameters

(p) in the model, is sometimes used for an estimate of the pure error variance . However, this expression is valid only if the model is adequate, and this has yet to be determined.

Another problem which is often encountered in liquid-liquid and vapour-liquid equilibria is that the equilibrium data sometimes exhibit heteroscedasticity, that is, the variance associated with data is not constant. If this is the case, weighted least squares or a transformation of the data may be required so that assumption 3 is followed.

In order to use weighted least squares, estimates of the pure error variance at each run location are required. From above it can be seen that these will rarely be available. When weighted least squares has been used it has generally been found that the point estimates of the parameters do not change much but the precision of the parameter estimates can be significantly different. Thus, when analyzing equilibrium data in which there is heteroscedasticity some type of transformation of the data may be required.

In this work the finding of heteroscedasticity was acknowledged but no data transformation was performed due to the number of models which exhibited this problem and because the primary objective was to develop methods that could be used to represent equilibrium data, not to develop statistically rigorous models to be used in these methods.

4.2 Model Choice and Discrimination

Due to time limitations totally rigorous model building could not be implemented. Some method, however, had to be developed for choosing appropriate models and for discriminating between models. The following criteria were chosen for choosing or discriminating between models.

1. Everything else being equal, model A was chosen over model B if its residual plots (plots of the residual vs. independent variables and vs. the predicted response variable) showed fewer trends than the residual plots for model B.
2. Everything else being equal, model A was chosen over model B if the SSR_A was "significantly" less than the SSR_B .
3. Everything else being equal, model A was chosen over model B if the individual 95 % confidence intervals for the parameters in model A were smaller than those for model B. If a confidence interval included zero parameters in the model were adjusted or dropped in order to obtain a simpler model with no significant increase in the SSR.
4. Everything else being equal, model A was chosen over model B if the correlations between the parameter estimates for model A were smaller than those for model B.

For two models with similar sums of squares, no trends in residual plots, similar confidence intervals for similar parameter values and reasonably similar parameter correlations between parameter values a method was required to choose between the models.

For linear (in the parameters) models there is a quantitative test called a Q-test which determines if an extra parameter in a model significantly improves the fit of this model. The Q-test involves determining the following quantity.

$$QQ = (SSR_A - SSR_B) / \hat{\sigma}^2 (p_B - p_A) \qquad \ldots(17)$$

where model B has the same form as model A but it has one or more extra parameters in it and $\hat{\sigma}^2$ is an estimate of the pure error variance. Under the appropriate assumptions QQ can be compared to an F-statistic with $(p_B - p_A)$ and $(n - p_B)$ degrees of freedom. If QQ is found to be larger than the F-statistic the extra terms in the model significantly improve the fit. This Q-test is really only valid for linear models that are adequate and have random errors that are normally distributed. For nonlinear models this method is not statistically valid. The statistically recommended procedure involves utilizing maximum likelihood functions and due to the large numbers of models that had to be tested the q-test provided a simple, quick method which, while not being statistically valid, provided some criterion for choosing between two models. Now that the methods of analyzing the models developed in this thesis have been explained the actual experimental results can be discussed.

4.3 Pure Component Equilibrium Concentrations

Methods for representing binary liquid-liquid equilibria enable one to predict binary organic phase concentrations from known aqueous phase concentrations. Since only one liquid-liquid extraction system was studied, the extrapolation of the results to other systems should only be attempted after further experimentation has shown that the methods developed in this work can be extended to other systems.

The first step in trying to develop methods for predicting organic phase concentrations from known or determined aqueous phase concentrations for the binary system of cobalt and nickel in D2EHPA involved

obtaining the pure component equilibrium data. As mentioned previously, other researchers in this field had shown that an increase in the temperature at which the extraction of cobalt and nickel was carried out resulted in an enhanced selectivity for cobalt over nickel when D2EHPA was used as the extractant. This enhanced selectivity was verified by comparing the equilibrium metal concentrations at temperatures of 25 and 60 ± 0.5 degrees Celsius.

Figures 1 and 2 show the pure component equilibrium extraction isotherms for cobalt and nickel respectively at 25 degrees Celsius. There appears to be virtually no difference between these two extraction isotherms. For a given aqueous phase metal concentration the pure component organic phase loading (concentration) was virtually identical for both metals. Both cobalt and nickel even had approximately the same maximum loading of 14.5 g/l.

From Figures 3 and 4 it can be seen that at 60 degrees Celcius the maximum nickel loading increased gradually to about 16 g/l while the maximum cobalt loading increased more dramatically to about 17 g/l. The cobalt isotherm at 60 degrees Celsius exhibited a much steeper increase in organic phase concentration as total metal concentration increased. This can be illustrated from the fact that at 60 degrees Celcius the organic phase cobalt loading reached 14 g/l with less than 1 g/l of cobalt in the aqueous phase while at the same temperature the nickel loading was only about 9 g/l at an aqueous phase concentration 1 g/l.

As other researchers had reported, it appeared that with D2EHPA, the increase in the selectivity of cobalt over nickel with an increase in

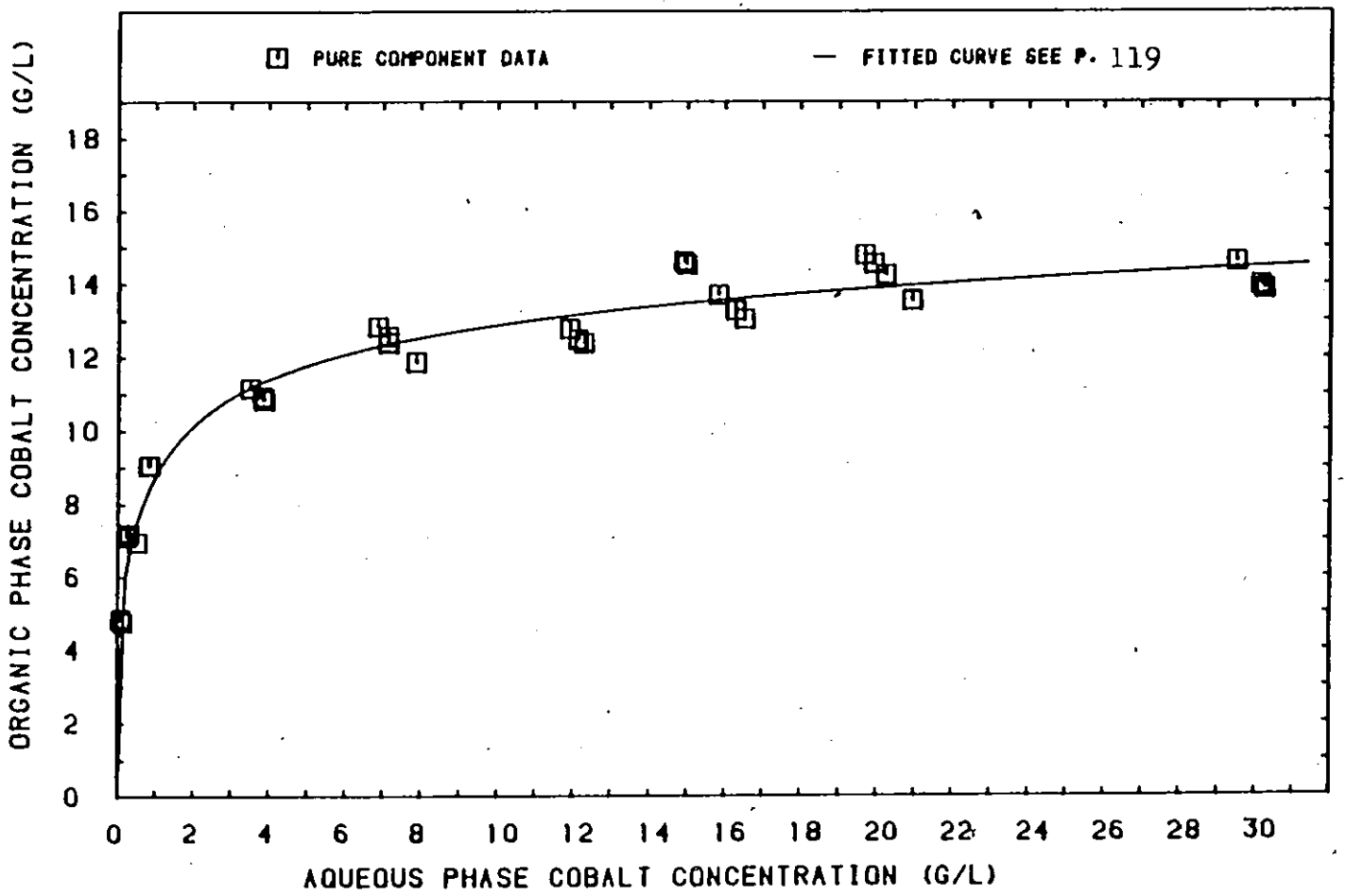


FIGURE 1. PURE COMPONENT COBALT EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.6-6.5.

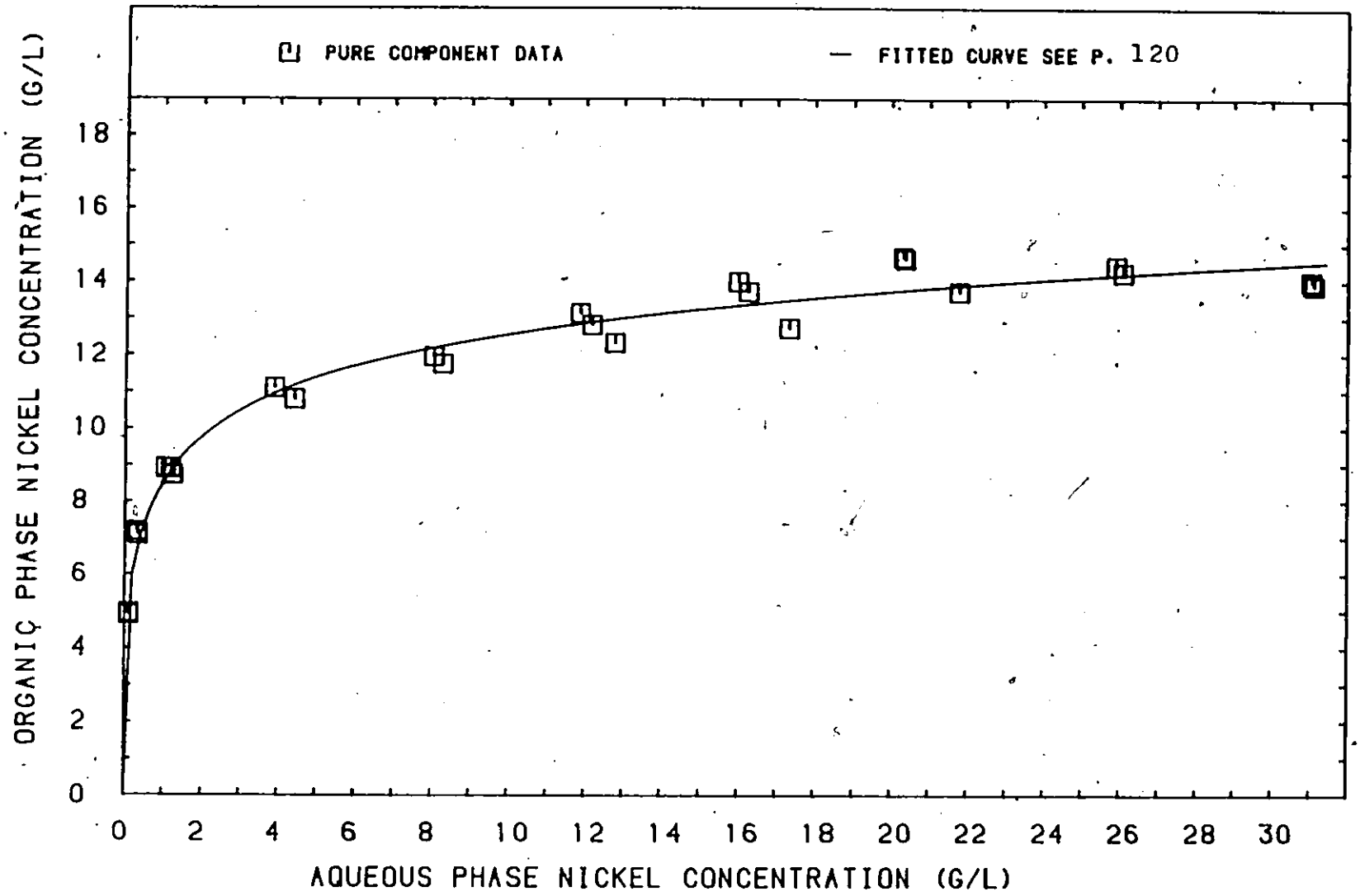


FIGURE 2. PURE COMPONENT NICKEL EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.6-6.4.

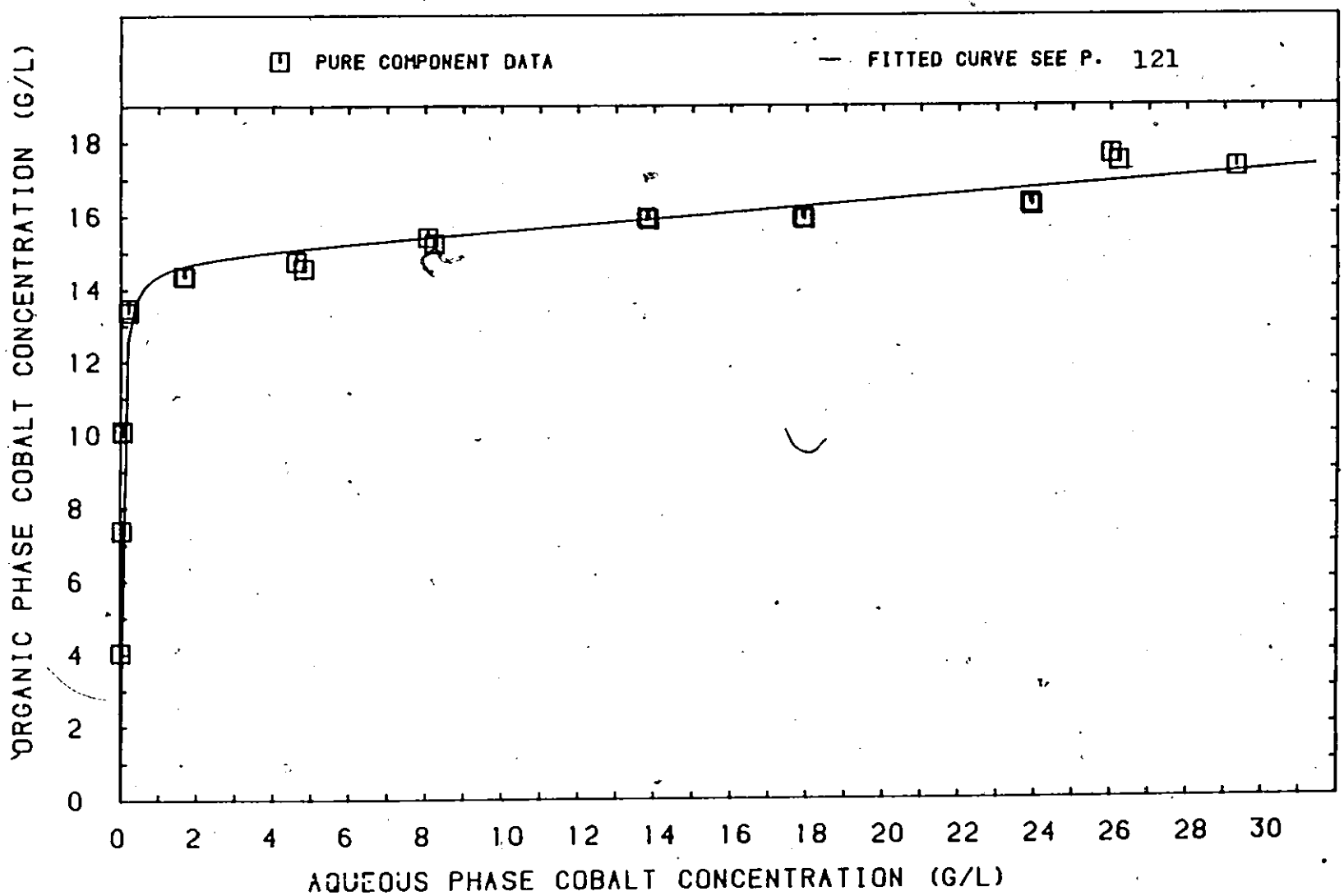


FIGURE 3. PURE COMPONENT COBALT EXTRACTION ISOTHERM AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.7-7.1.

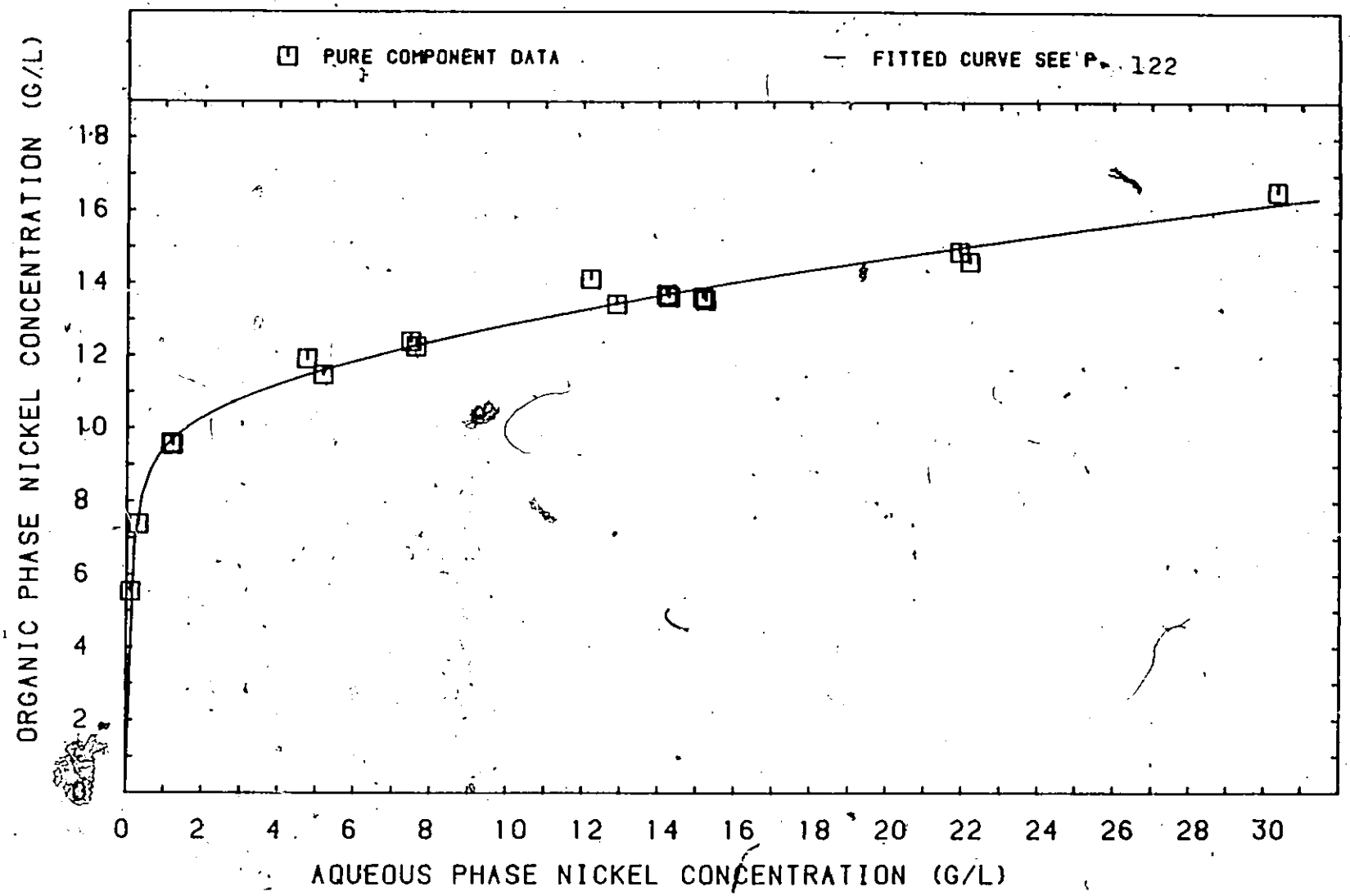


FIGURE 4. PURE COMPONENT NICKEL EXTRACTION ISOTHERM AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 6.0-6.8.

temperature may have been due to some change in the cobalt extraction process since there appeared to be much less change in the nickel extraction isotherm compared to the cobalt isotherm as the temperature was increased from 25 to 60 degrees Celcius.

The curves drawn through the experimental data points in Figures 1 through 4 were obtained by fitting the equilibrium data to the following equation which is a combination of the Freundlich and Langmuir isotherms. It should be noted that X' and Y' are equilibrium aqueous and organic phase concentrations in g/l.

$$Y' = \theta_1\theta_2X' / (1+\theta_2X') + \theta_3X'^{\theta_4} \qquad \ldots(18)$$

Initially the data were fit to each isotherm separately. In some cases however, the residual plots showed trends which suggested that the models were inadequate so the combination equation was used. Some of the fitted parameter estimates with the four parameter equation had individual 95 % confidence intervals that contained zero. For this reason some of the parameters were "removed" from the model by setting them to a value of one. This resulted in various three parameter models that were all forms of the "parent" equation.

The chosen model forms, the associated parameter estimates, their 95 % confidence intervals and the correlations between parameter estimates, for these and for other models used in this thesis, can all be found in Appendix C. Plots of the actual "dependent" or response variable versus the predicted "dependent" variable are often useful in

judging the fit of a regression model. Generally, the closer the points are to the line y = x (actual = predicted) the better the fit. For this reason, for each fitted model a plot of the actual response value (ACT.) versus the predicted response value (PRED.) was made. These can be found in Appendix F along with the residual plots. In general one usually examines the residuals versus the "independent" variables, the predicted response variable and the run order. Only the first two types were deemed necessary for this work. Residuals are not usually plotted versus the actual response variable because they are correlated with this variable (55).

Due to the large number of figures in this thesis a method was required to organize them in an "easy to use" fashion. All supplementary figures like residual plots and plots of ACT. vs. PRED. have the same first number as their corresponding main figure and in addition they have letters and additional numbers, if required, to further classify them. For example, for Figure 1., the ACT. vs. PRED. plot is denoted as Figure 1A. while the residual vs. aqueous phase concentration is denoted as Figure 1B. With this clarification, the remainder of the results can now be discussed.

For the pure component isotherms there were only two residual plots that gave reason for concern. The residual plots for the pure component cobalt extraction isotherm at 60 degrees Celsius. (Figures 3B and 3C) showed that this data exhibited heteroscedasticity. For aqueous phase cobalt concentrations less than 1 g/l the magnitude of the residuals was significantly higher than that for the other concentrations. This was largely due to the sharp, almost vertical rise in organic phase con-

centration at low aqueous phase concentrations. The only real option in terms of alleviating this problem of heteroscedasticity for this particular model appeared to be applying weighted least squares but as mentioned previously this was not possible due to the lack of an estimate for the pure error variance.

4.4 The Collection of Binary Equilibrium Data

The first method to represent the binary equilibria for the cobalt/nickel extraction was a method which would enable one to use a McCabe-Thiele type of approach in order to estimate the number of ideal extraction stages required for a given separation. This method also governed the manner in which the equilibrium data were collected. Graphs in which the organic phase concentration of one metal were obtained at a constant aqueous phase concentration of the other metal would enable one to perform the classical stepping off of stages that is characteristic of the McCabe-Thiele approach.

For this reason experiments for obtaining the binary data were performed in such a way as to try to obtain a constant aqueous phase equilibrium concentration for each individual metal. For example, a range of equilibrium organic and aqueous phase cobalt concentrations were obtained at constant aqueous phase nickel concentrations. Four different organic/aqueous phase cobalt extraction curves were obtained for the case where the equilibrium aqueous phase nickel concentration was approximately 3 g/l, 6 g/l, 12g/l and 24 g/l respectively. The same procedure was implemented for the nickel extraction as a function of approximately 3, 6, 12, and 24 g/l of cobalt in the aqueous phase at

equilibrium. These constant aqueous phase concentrations had to be obtained within a reasonably small range so that reasonable predictions could be made. It was decided that 5 % was the maximum deviation that would be allowed. This resulted, for example, in the need to obtain aqueous phase concentrations between 2.85 and 3.15 g/l for the "constant" 3 g/l aqueous phase metal concentration. This proved to be rather painstaking work as it basically involved a trial and error procedure in which the amount of initial cobalt and nickel that was added to a given flask had to be adjusted until the equilibrium concentrations were within the desired 5 % of the chosen concentrations. This was even more difficult because the sodium correction factor had to be taken into account.

The results for the binary equilibrium of cobalt and nickel at 25 degrees Celsius are shown in Figures 5 and 6 respectively. In general, as the equilibrium aqueous phase concentration of metal B increased the organic phase concentration of metal A decreased. This is true in all cases for the nickel extraction isotherms as a function of the aqueous phase cobalt concentration. From Figure 5 it can be seen that the cobalt extraction isotherms are not as well behaved since at high aqueous phase cobalt concentrations (> 12 g/l) and relatively low aqueous phase nickel concentrations (~3 g/l) the binary organic phase cobalt concentrations were either greater than or indistinguishable from the pure component organic phase cobalt concentrations. These values may be such that the low concentration of nickel does not significantly inhibit the extraction of cobalt and/or that small amounts of nickel might actually enhance the uptake of cobalt at these high cobalt concentrations. It

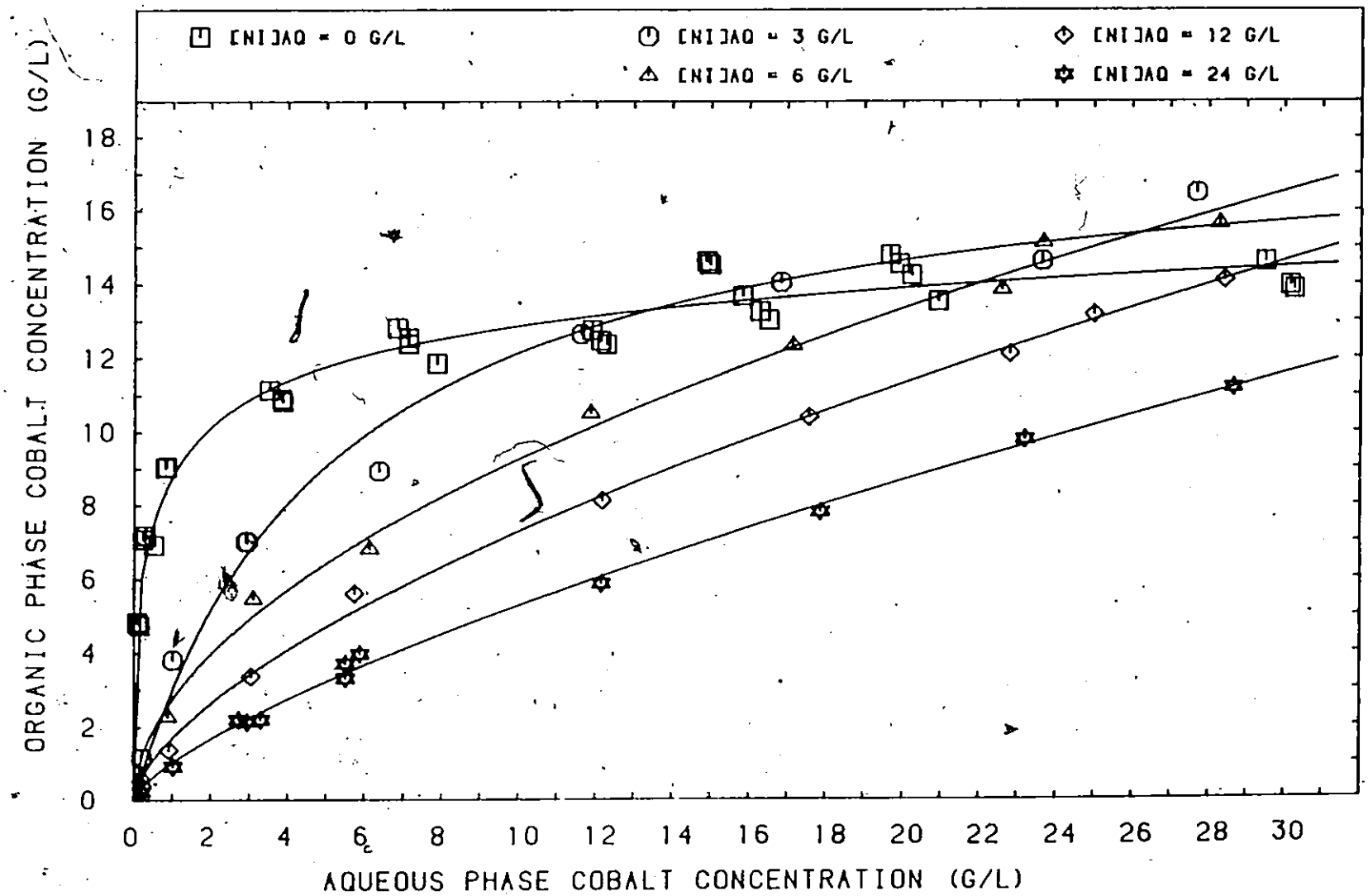


FIGURE 5. TWO COMPONENT COBALT EXTRACTION ISOTHERMS AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.3.

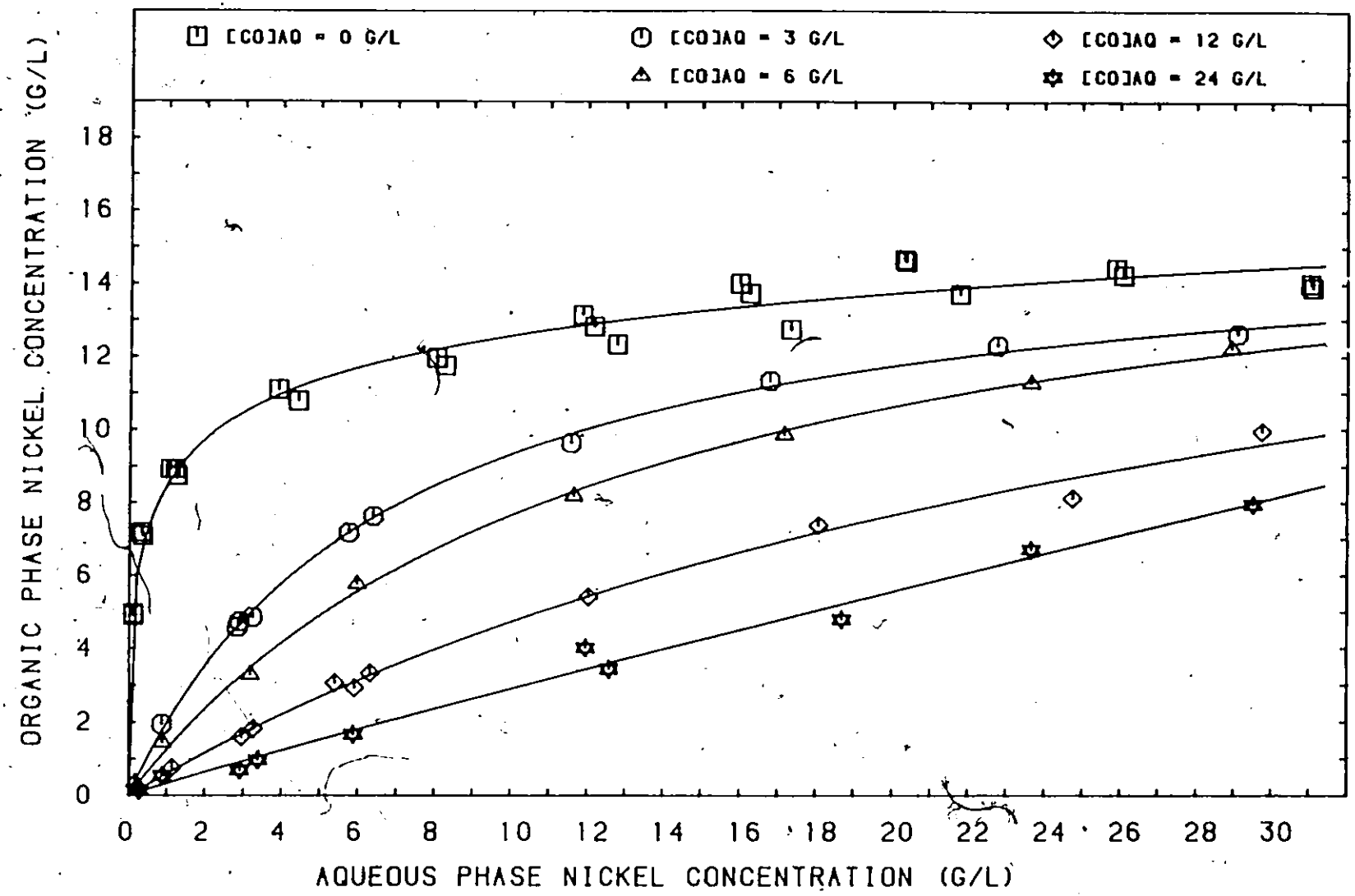


FIGURE 6. TWO COMPONENT NICKEL EXTRACTION ISOTHERMS AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

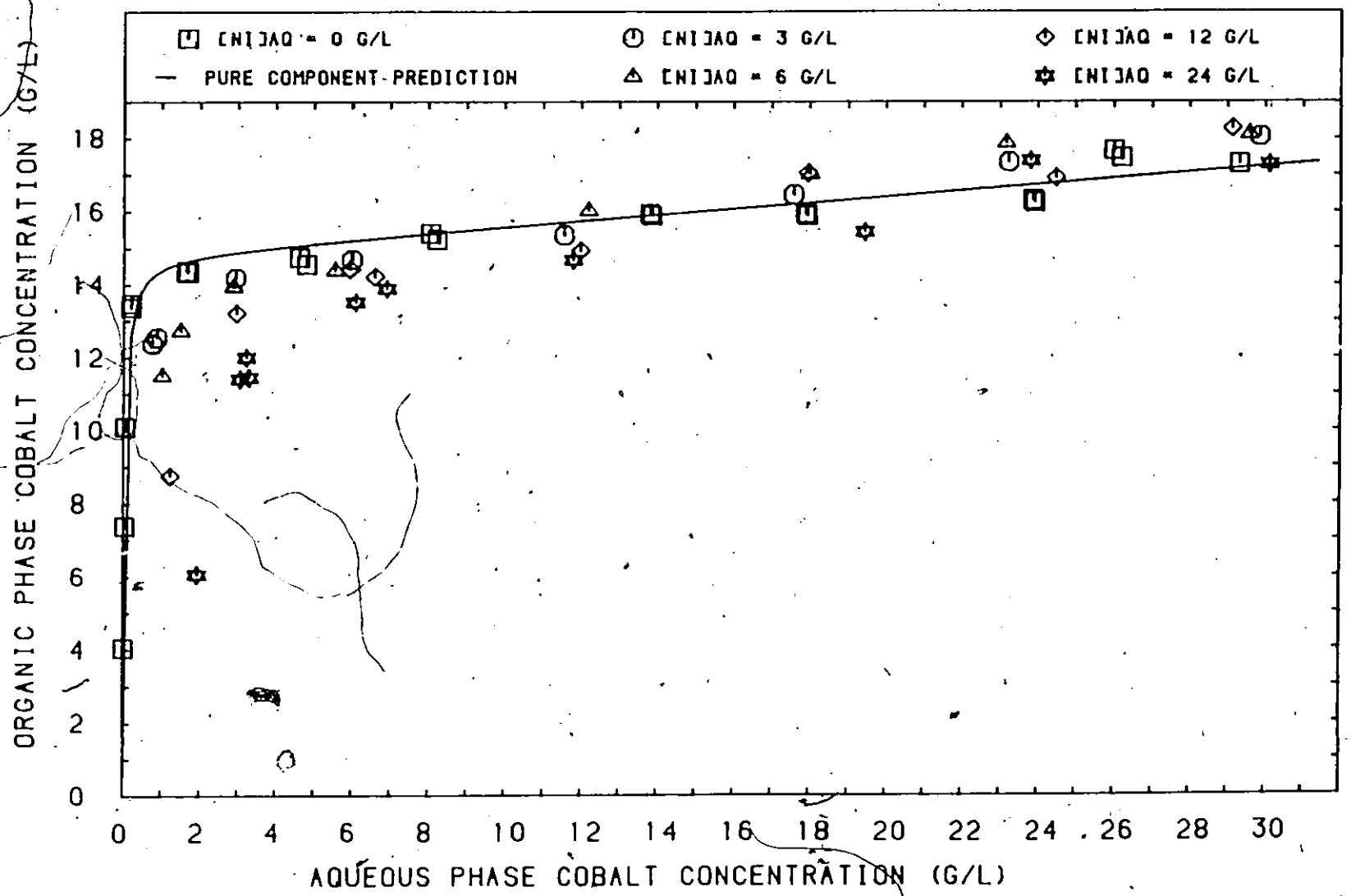


FIGURE 7. TWO COMPONENT COBALT EXTRACTION ISOTHERMS AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

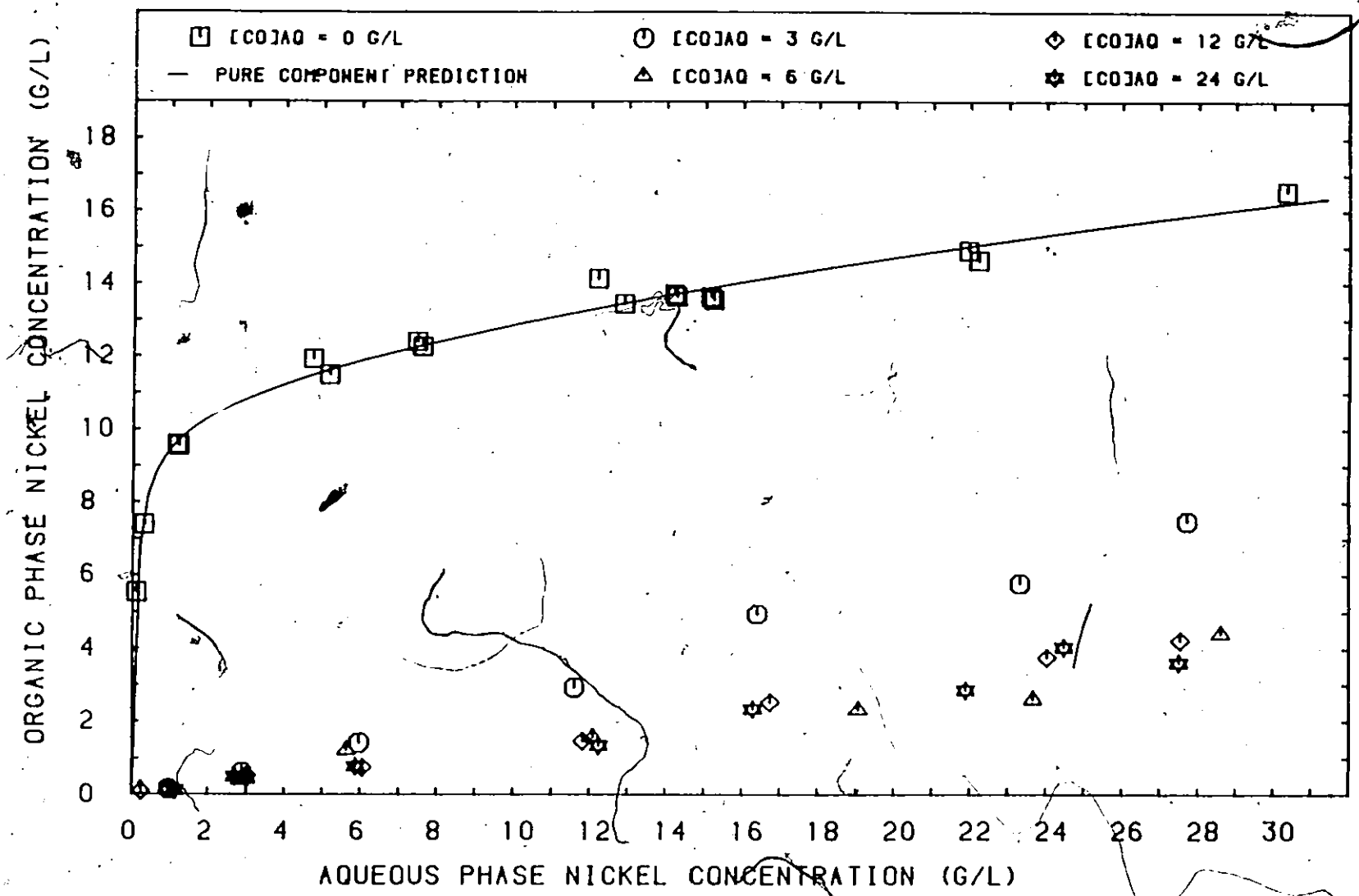


FIGURE 8. TWO COMPONENT NICKEL EXTRACTION ISOTHERMS AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

is not clear if the organic phase concentrations in question are significantly greater than the pure component concentrations. In any case, a practical extraction process would not likely be carried out where the aqueous phase equilibrium cobalt concentrations were greater than 15 g/l since the aqueous stream would need to be continuously recycled to eventually remove most of the cobalt. Data were obtained in this region to see if, and when, a maximum loading would be reached.

The equations and parameter values for each of the curves in Figures 5 and 6 can be found in Appendix C . The binary curves could be reasonably well represented by either a Langmuir or Freundlich isotherm. The combination equation did not appear to be required. The residual plots and plots of ACT. vs. PRED. can be found in Appendix F. There did not appear to be any trends in any of these residual plots.

The real effect that an increase in temperature has on the selectivity of cobalt over nickel with D2EHPA can be seen from Figures 7 and 8. These show the binary equilibrium data for cobalt and nickel respectively at 60 degrees Celcius. The same constant aqueous phase concentrations were used as in the binary curves at 25 degrees Celsius. From Figure 7 the presence of large amounts of nickel can be seen to have only a very small effect on the extraction of cobalt. Even at an aqueous phase nickel concentration of 24 g/l the organic phase cobalt concentration does not appear appreciably different from the pure component isotherm (at least for greater than 8 g/l of cobalt in the aqueous phase). Figure 8 shows the reverse trend such that a small amount of cobalt in the aqueous phase greatly inhibits the nickel loading. It

should be noted that in order to achieve a concentration of 3 g/l of cobalt in the aqueous phase more than 9 g/l of cobalt would be found in the organic phase.

For an equilibrium aqueous phase nickel concentration of 20 g/l the addition of enough cobalt to produce an aqueous phase cobalt concentration of just 3 g/l resulted in a drop in the organic phase nickel concentration from 14 g/l to 6 g/l. This compares to a drop from 14 g/l to about 11 g/l for nickel under the same conditions except at a temperature of 25 degrees Celsius. Not only do these figures show the extent of the enhanced selectivity of D2EHPA for cobalt over nickel at higher temperatures but they also show a tremendous flaw in the use of this method for representing binary equilibrium data in order to utilize a McCabe-Thiele type of approach.

From the extraction chemistry section it should be obvious that D2EHPA is far from being the best extractant for separating cobalt from nickel. Yet, for D2EHPA at 60 degrees Celcius, to develop cobalt or nickel isotherms at constant other metal aqueous phase concentrations requires extremes in concentrations of the other metals in order to differentiate between the curves. For extractants like PC88A and CYANEX 272, extractants which hold much more commercial promise than D2EHPA, obtaining reasonably different binary extraction isotherms at constant other metal aqueous phase concentrations might require concentrations greater than the solubility limits for cobalt and nickel sulphates. For this reason this method was rejected for representing equilibrium data since it clearly fails at, what one would consider, practical conditions. With the failure of this method, the method used by Ioannou et. al. (52) was investigated further.

4.5 The DELTA Y Method

The method used by Ioannou et. al. to correlate multicomponent data for lanthanide elements was explained briefly in the literature review section. Their method made use of analogies to vapour-liquid equilibrium and involved the use of equation (16). From this equation the deviations from "ideality" or the ΔY (DELTA Y) values were defined such that

$$\Delta Y_A = Y_A - Y_A^* x_A \qquad \ldots(19)$$

where Y_A was the organic phase metal concentration for component A in a binary system containing A and B in units of gmol/l, Y_A^* was the expression for the pure component organic phase equilibrium concentration of component A, also with units of gmol/l and x_A was the mole fraction of component A on a solvent free basis. From their experimental data they determined equations for the pure component concentrations such that the Y_A^* values were correlated by the totally empirical equation given below.

$$Y_A^* = \mu_1 X_A^{\mu_2} \exp(\mu_3 H^W) \qquad \ldots(20)$$

where $W = \mu_4 + \mu_5 H + \mu_6 H^2$, X_i was the aqueous phase pure metal concentration in gmol/l, H was the hydrogen ion molar concentration and all μ_i were parameters. For constant total aqueous phase metal concen-

tration and constant pH the ΔY_i values were correlated by another empirical equation which is given below.

$$\Delta Y_A = \eta_1 x_A^{\eta_2}(1-x_A)^{\eta_3}\exp(\eta_4 H) \qquad \ldots(21)$$

where the η_i's were parameters and x_i was the mole fraction (on a solvent free basis) of component i. Thus substituting correlations (20) and (21) into (16) they could determine Y_T for a given aqueous phase composition. The organic phase component concentrations were determined from equation (22) where the separation factor, SF, was given by $SF_{A,B} = Y_A X_B / Y_B X_A$

$$Y_A = Y_T / (1 + (X_B / SF_{A,B} X_A)) \qquad \ldots(22)$$

Thus using this method, Ioannou et. al. could predict organic phase concentrations from a knowledge of aqueous phase compositions and the separation factor.

There were a number of questionable practises carried out by these authors. The authors appeared to bypass their correlation for DELTA Y by introducing the separation factor in their equations. Why they didn't rearrange equation (19) and solve for Y_i directly could not be determined. This would have reduced the number of calculations and would not have required the use of an average separation factor which can change by orders of magnitude, depending on the conditions used

to determine it. It appears even more suspect when one attempts to follow their example calculation and one notices that the value they determined for their arithmetic average separation factor was not the value they used in their sample calculation. Thus their method could best be summed up as follows. They correlated their pure component equilibrium data with a 6 parameter model (which was very nonlinear in the parameters). They correlated their DELTA Y function with a nonlinear equation involving 4-5 parameters . Using these two correlations they then needed to apply an average separation factor (which wasn't in fact the average value they obtained) to obtain less than a 6 % error between their actual and predicted values. Their method was further restricted in that it was performed, and appeared to be valid, only at the constant total aqueous phase metal concentrations and the constant pH values used by the authors. Ioannou et. al. claimed the results could be linearly interpolated for cases where the total metal concentration was not equal to one of the two values that they used in their experiments.

With these problems outlined, a relatively apprehensive approach was undertaken to determine whether or not their DELTA Y function could be used effectively as a method to correlate binary equilibria (at least for the separation of cobalt and nickel with D2EHPA). Modifications were made in an attempt to alleviate some of the limitations of their method..

The following points should be noted. In their case they included an expression for the hydrogen ion concentration in their pure component expression and in their correlation for DELTA Y. In the present work, the experiments were carried out at a high enough pH that the pH had a negligible effect on the equilibrium concentrations.

Since the experimental data in this work had been collected with the McCabe-Thiele approach in mind the experimental data was already separated according to aqueous phase metal concentrations. Instead of trying to separate the data into groups with similar total metal concentrations, equations were developed which tried to incorporate the actual individual aqueous phase concentrations.

As mentioned previously, the pure component equilibrium concentrations were fit to a combination Freundlich and Langmuir isotherm involving three parameters. The appropriate ΔY functions were calculated according to equation (19) and are shown in Figures 9, 10, 11 and 12. It should be pointed out that from the definition of DELTA Y, at $x_A = 0$ and at $x_A = 1.0$, $\Delta Y_A = 0$.

For a temperature of 25 degrees Celcius the DELTA Y functions do not show very specific trends. The cobalt DELTA Y curve for $0 < x_{Co} < 0.4$ follows a curve with very little spread in the data. Over this mole fraction range the aqueous phase nickel concentration appears to have had little effect on the DELTA Y function. However for $x_{Co} > 0.4$ the data spreads out and appears to be a function of the actual aqueous phase nickel concentration although no clear pattern could be seen.

For the nickel DELTA Y function (Figure 10) the data appear to behave in a slightly parabolic fashion but again there is a large random spreading of this data (more so than for the cobalt DELTA Y function) and no specific trends corresponding to different aqueous phase cobalt concentrations could be seen.

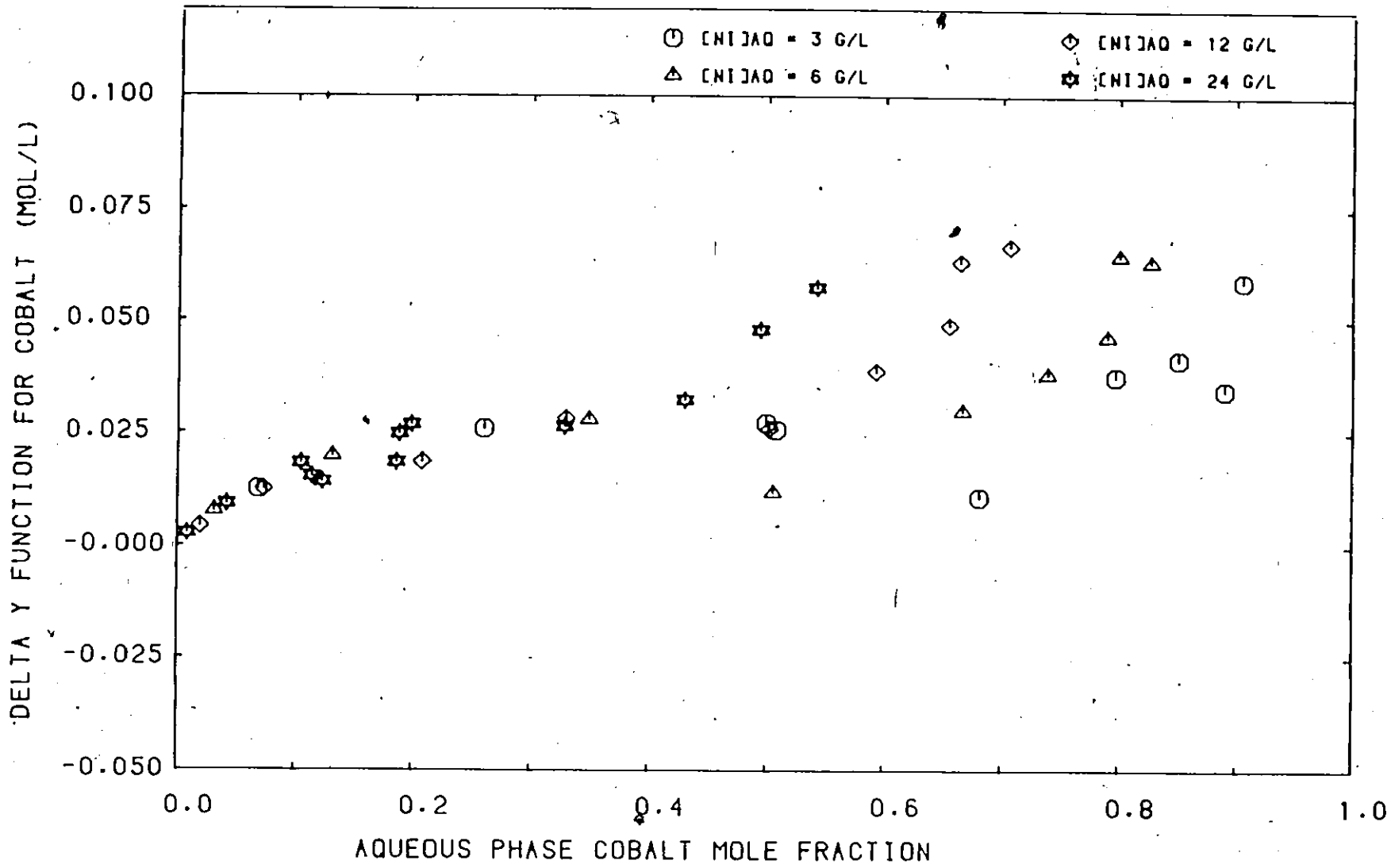


FIGURE 9. DELTA Y FUNCTION FOR COBALT AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

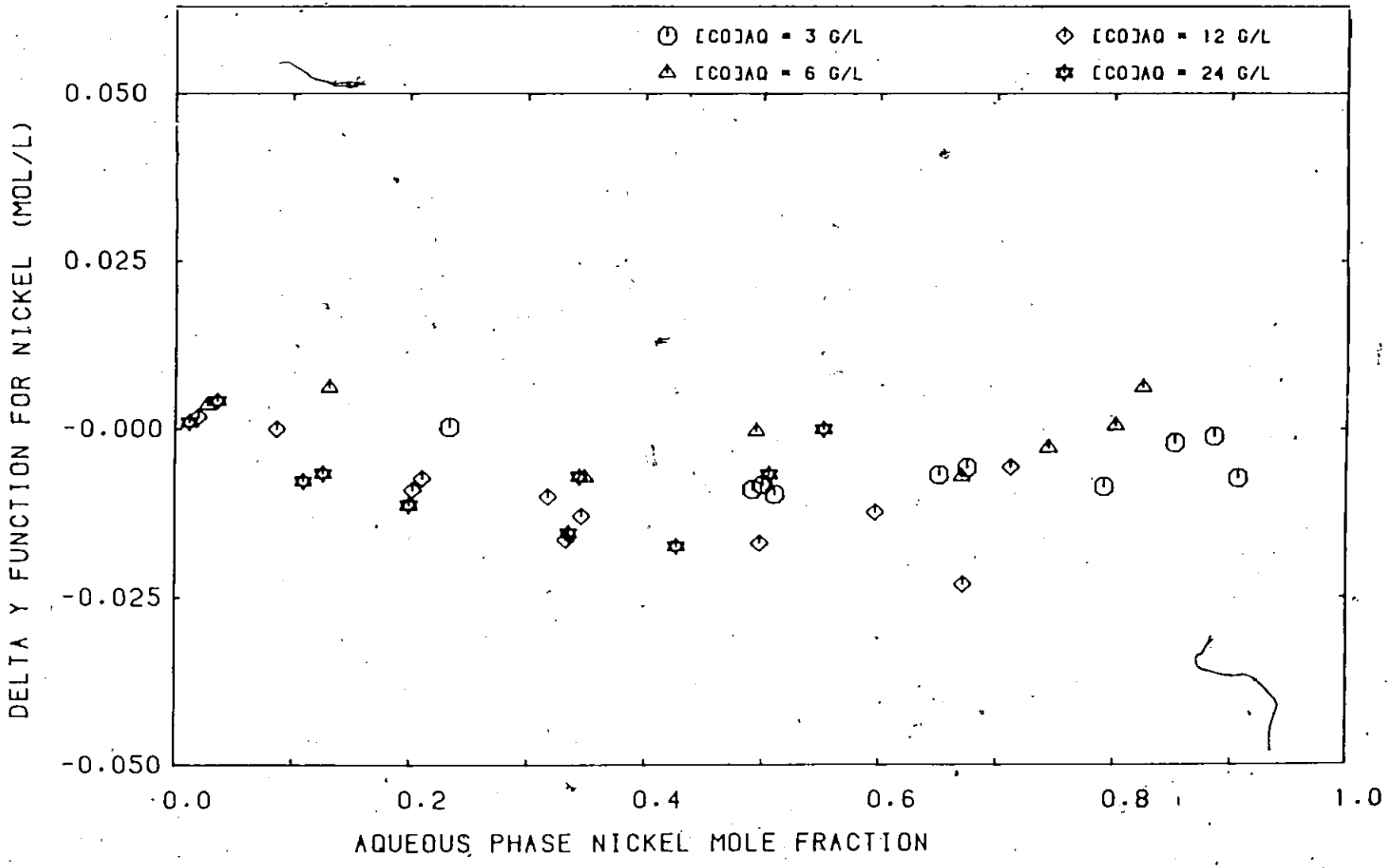


FIGURE 10. DELTA Y FUNCTION FOR NICKEL AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.3.

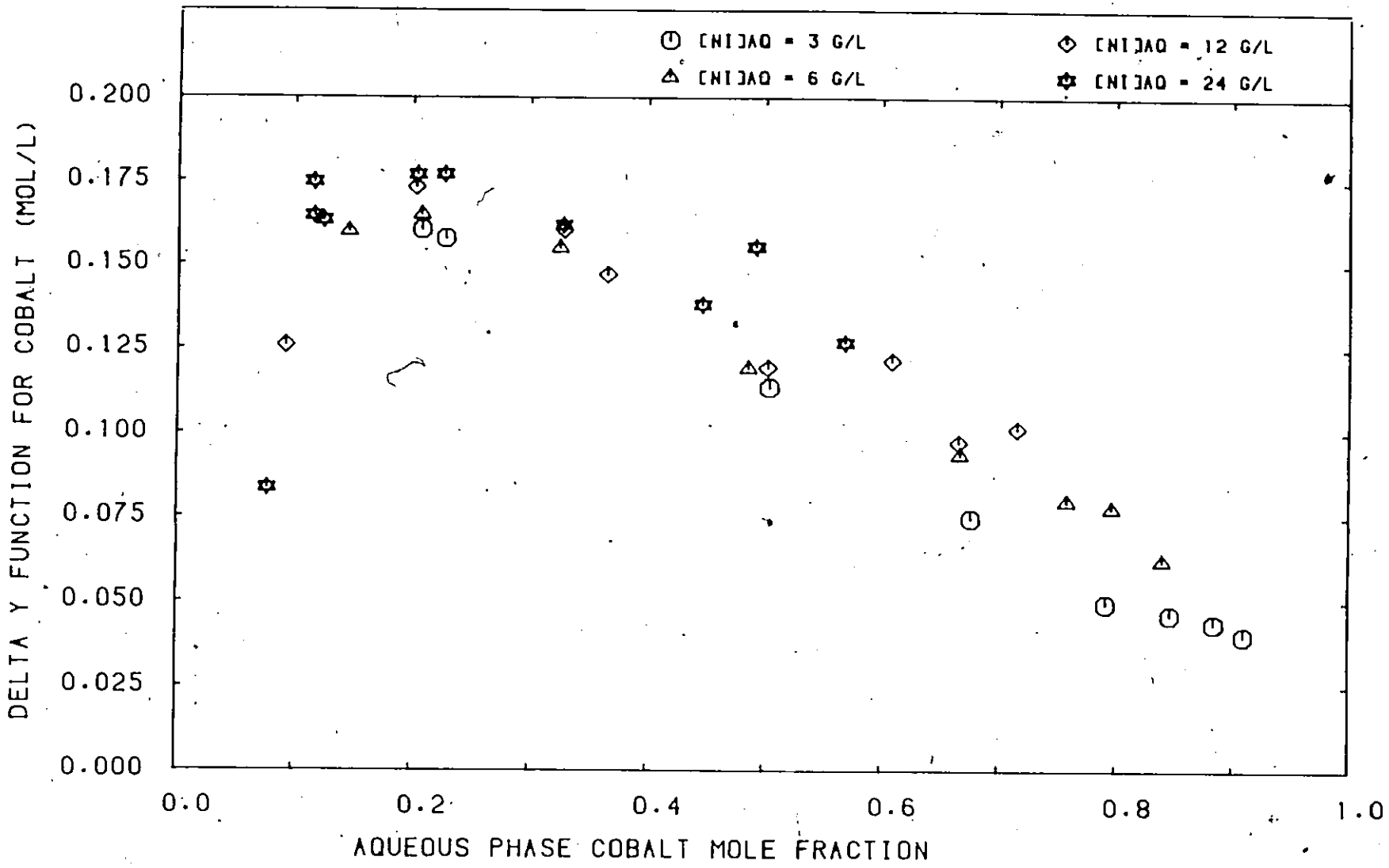


FIGURE 11. DELTA Y FUNCTION FOR COBALT AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

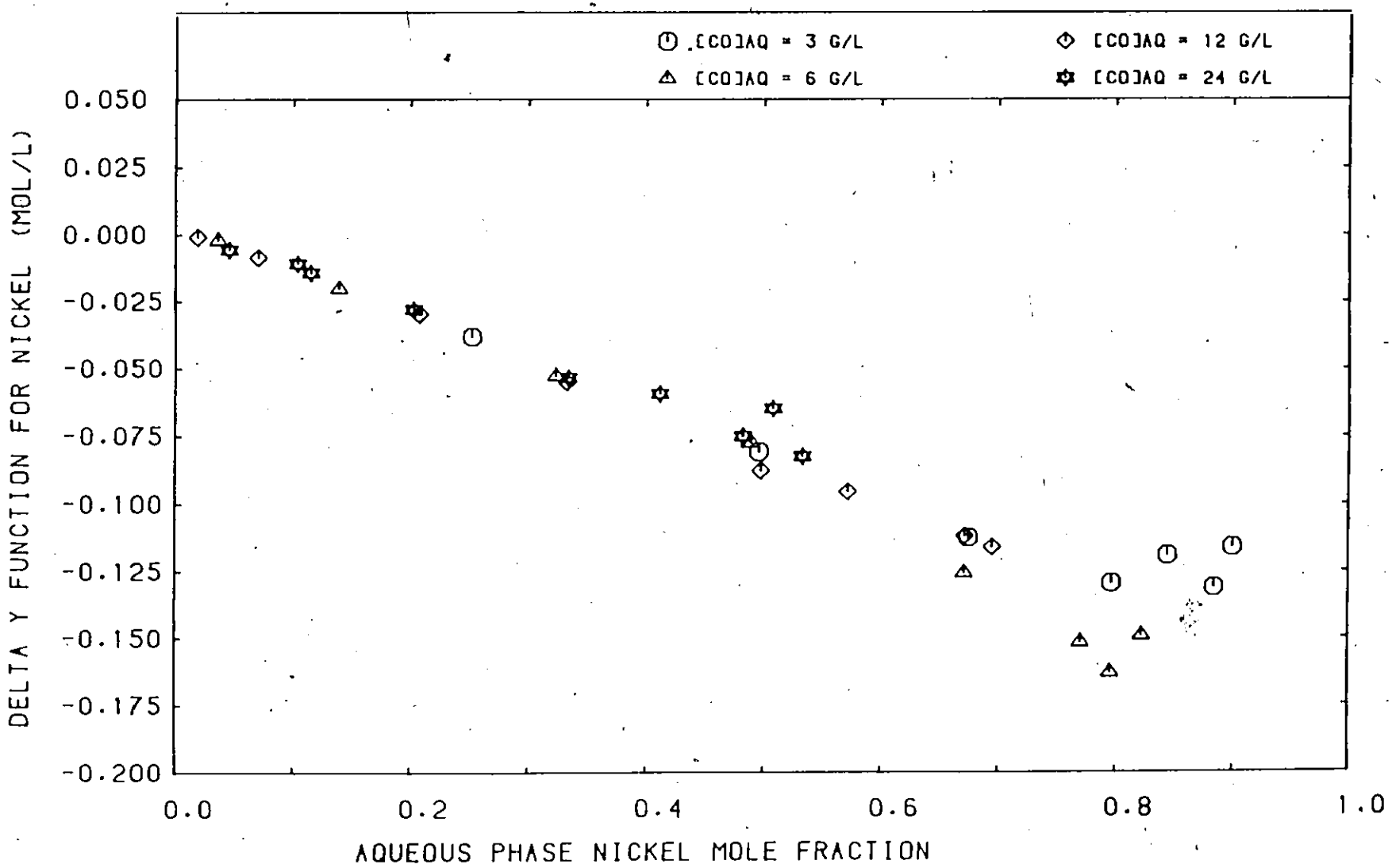


FIGURE 12. DELTA Y FUNCTION FOR NICKEL AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

From Figures 9 and 10 it is evident that the magnitude of DELTA Y is very small. In fact the extraction of cobalt and nickel at 25 degrees Celsius is close to being "ideal" according to the convention used by Ioannou et. al.. With the relatively large error in the experimental procedure it is difficult to determine if the DELTA Y values at 25 degrees Celcius are significantly different from zero. The small trends and the relatively large spread in the DELTA Y functions, especially for nickel, may in fact be due to the error in curve fitting the pure component data since this error is of a similar magnitude as the magnitude of DELTA Y at 25 degrees Celsius.

Figures 11 and 12 (the DELTA Y functions for cobalt and nickel respectively at 60 degrees Celcius) show more pronounced effects. They appear much more concave or convex in shape than their corresponding curves do at 25 degrees Celsius. The magnitudes of DELTA Y are also much larger at 60 degrees than at 25 degrees and are clearly much greater than the error associated with the pure component curve fitting. It can be seen from Figures 11 and 12 that there is a lack of data at the end points of both curves where it would seem that more data should have been collected. In both these cases the effect of the aqueous phase metal concentration of one metal does not appear to show significant trends in the DELTA Y functions of the other metal.

Models similar to those used by Ioannou et. al. were used to try to adequately correlate the DELTA Y functions. This general model class is given below.

$$\Delta Y_A = \beta_1(1-x_A)^{\beta_2} x_A^{\beta_3} X'^{\beta_4}_B + \beta_5(1-x_A)x_A X'^{\beta_6}_B \qquad \ldots(23)$$

where the X'_B is the aqueous phase concentration of component B in g/l . The parameter values can be found in Appendix C along with the usual information about the parameters. The above type of model was used due to the end point requirements of the DELTA Y function. It can be seen that the "other metal" aqueous phase concentration was incorporated in the model but from the final choices of the parameter values it can be seen that some of these terms were not significant in some of the cases.

For the cobalt DELTA Y function at 25 degree Celsius the plot of ACT. vs. PRED. (see Appendix F, Figure 9A) showed considerable deviation from the straight line of Actual = Predicted. While the residual plots for this curve were relatively random, a good case could be made for heteroscedastic behaviour in the residual vs. aqueous phase mole fraction diagram (Appendix F, Figure 9B). For the DELTA Y function for nickel at 25 degrees Celsius (Figure 10), the large spread in the data resulted in a plot of ACT. vs. PRED. (Figure 10A) which showed virtually no correlation between these two values. The residual plots appear totally random except for Figure 10B in which the end points appeared to be underestimated or overestimated.

For cobalt at 60 degrees Celsius the ACT. vs. PRED. plot (Figure 11A) tended to show a reasonably good fit. The residual plot showed no significant trends except for the plot vs. the aqueous phase cobalt mole fraction (Figure 11B). At low mole fraction values the magnitude of 1 residual appears to be significantly larger than the others. This is not an outlier but has to do with the poor selection of concentrations in the experiments. Since few data points were obtained at low cobalt mole

fraction values at 60 degrees Celsius, the experimental model is "biased" towards the other data points. If this form of model is deemed adequate the estimated parameter values would likely be significantly different if more data points were obtained at low mole fractions.

The predicted model for the nickel DELTA Y function (Figure 12A) shows reasonably good trends in the ACT. vs. PRED. plots but the residual plots appear to show that the model is inadequate. Heteroscedastic behaviour and a specific sinusoidal trend were evident as the nickel aqueous phase mole fraction decreased. Many variations of equation (23) were tried but the model given in Appendix C was the best model that could be found. The actual results, in terms of how well the DELTA Y method predicted the organic phase concentrations, will be discussed in a later section after all the different approaches to the problem of representing binary equilibrium have been examined.

4.6 The MOLE FRACTION Method

The next method to correlate equilibrium data was discovered by accident. In the attempts to develop appropriate ways of modelling the DELTA Y function a multitude of plots were made to try to find some type of trend that could be easily represented. During this plotting a plot of the organic phase cobalt mole fraction (on a solvent free basis) was made against the aqueous phase cobalt mole fraction (also on a solvent free basis). The results can be seen in Figure 13. At 25 degrees Celcius the data can be seen to follow a relatively smooth curve with only minor deviations from it. For the 60 degree Celcius curve the data has more spread in it but it follows a reasonably good trend. Lu et.

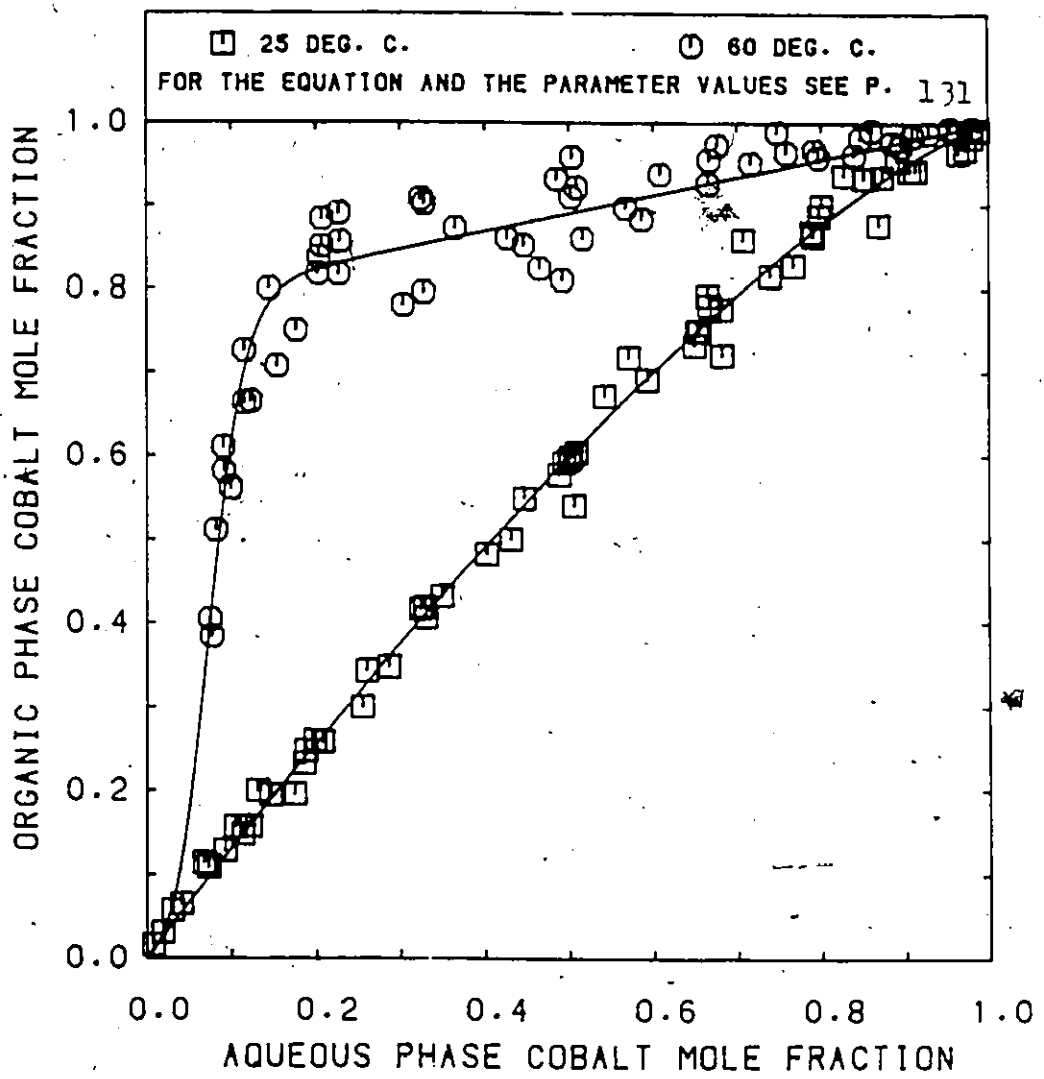


FIGURE 13. COBALT MOLE FRACTION DIAGRAM ON A SOLVENT FREE BASIS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH AT 25 DEG. C. = 5.3-6.4
EQUILIBRIUM PH AT 60 DEG. C. = 5.5-6.4; A/O = 1.

al. (56) suggested the following form of equation for modelling vapour-liquid equilibria.

$$y_A / y_B = x_A(Cx_A + Ex_B) / x_B(Fx_A + x_B) \qquad \ldots(24)$$

where C, E, and F were parameters. This equation was found to represent the data at 25 degrees quite well but it was clearly inadequate to represent the data at 60 degrees Celsius. A number of different modifications were made to this equation until equation 25 was developed.

$$y_A = (x_A + \lambda_1(x_A^2 - x_A)) / (x_A + (1-x_A)^{\lambda 2}) \qquad \ldots(25)$$

Of the models that were tried, the above two parameter model was found to be the "best". The parameter estimates can again be found in Appendix C while the residual plots can be found in Appendix F. At 25 degrees Celcius the residual plots were relatively random but problem areas were again found at the end points where the model appeared to overestimate (as x_{Co} approached 1.0) and underestimate (as x_{Co} approached 0). Even though the actual deviations from the line actual = predicted were small, inadequacies in the model were definitely present.

The 60 degree Celcius mole fraction diagram had a similar problem as x_{Co} approached 1.0. In this area the model consistently predicted high. At other concentrations the pure error variance increased rather

dramatically. It is quite possible that the organic phase mole fractions do not just depend on the aqueous phase mole fractions, but more explicitly, on the actual aqueous phase concentrations.

Only after getting this far with the MOLE FRACTION method did the question arise as to how to determine the actual organic phase metal concentrations as opposed to the mole fractions. In vapour-liquid equilibria one usually knows the total pressure of the system. This enables one to determine the vapour phase compositions. However, in liquid-liquid extraction applications the corresponding total organic phase metal concentration can only be estimated and this can only be done in limited situations in which one knows the total metal concentration going into an extraction process. By measuring the aqueous phase concentrations one could estimate the total organic phase metal concentration by mass balance and from this one could use a mole fraction diagram to estimate the individual organic phase metal concentrations.

The final method that was used to try to adequately represent the binary cobalt/nickel equilibrium data was developed after noting the somewhat sucessful attempts in making analogies to vapour-liquid equilibria. If Ioannou et. al.'s DELTA Y method could be used in liquid-liquid extraction to describe "non-ideal" systems why not use a method that more closely corresponds to the vapour-liquid treatment of non-ideal systems.

4.7 The PSEUDO GAMMA Method

For the case in vapour-liquid equilibria in which one has a non-ideal solution but an ideal vapour phase the following equation is valid.

$$y_i = x_i P_i^* \gamma_i / P_T \qquad \ldots(26)$$

where all the variables were defined as before and where γ_i is the activity coefficient for component i.

Making analogies similar to those made by Ioannou et. al. in the DELTA Y treatment the following equation was developed.

$$Y_i = y_i Y_T = x_i Y_i^* \gamma s_i \qquad \ldots(27)$$

where γs_i is called the PSEUDO GAMMA function. In no way does this represent the activity coefficient for the system. As previously mentioned there have been few cases in which the activity coefficients for liquid-liquid systems have been estimated and these were found to be valid for only dilute systems which were not of practical importance.

The proposed method for predicting the organic phase concentration from known aqueous phase concentrations is as follows;

1. Calculate Y_{Ni}^* and Y_{Co}^* from the Langmuir-Freundlich composition equation (see equation (18)).
2. Calculate γs_i from a rearranged version of equation (27).
3. Develop appropriate models for the PSEUDO GAMMA function in terms of the aqueous phase compositions.
4. Predict the actual organic phase concentrations from a knowledge of the aqueous phase compositions and the estimated PSEUDO GAMMA function.

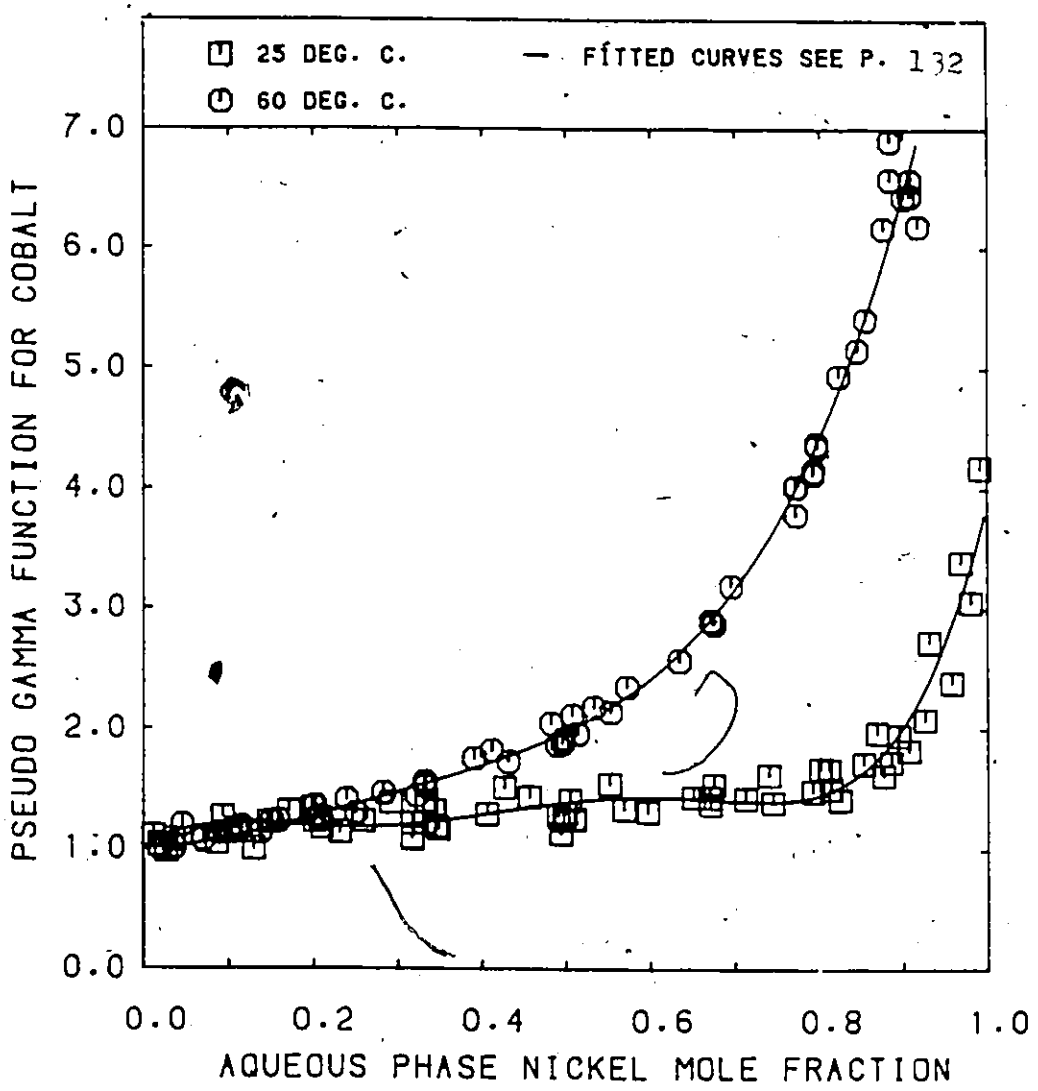


FIGURE 14. PSEUDO GAMMA FUNCTION FOR COBALT

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH AT 25 DEG. C. = 5.3-6.4.
EQUILIBRIUM PH AT 60 DEG. C. = 5.5-6.4; A/O = 1.

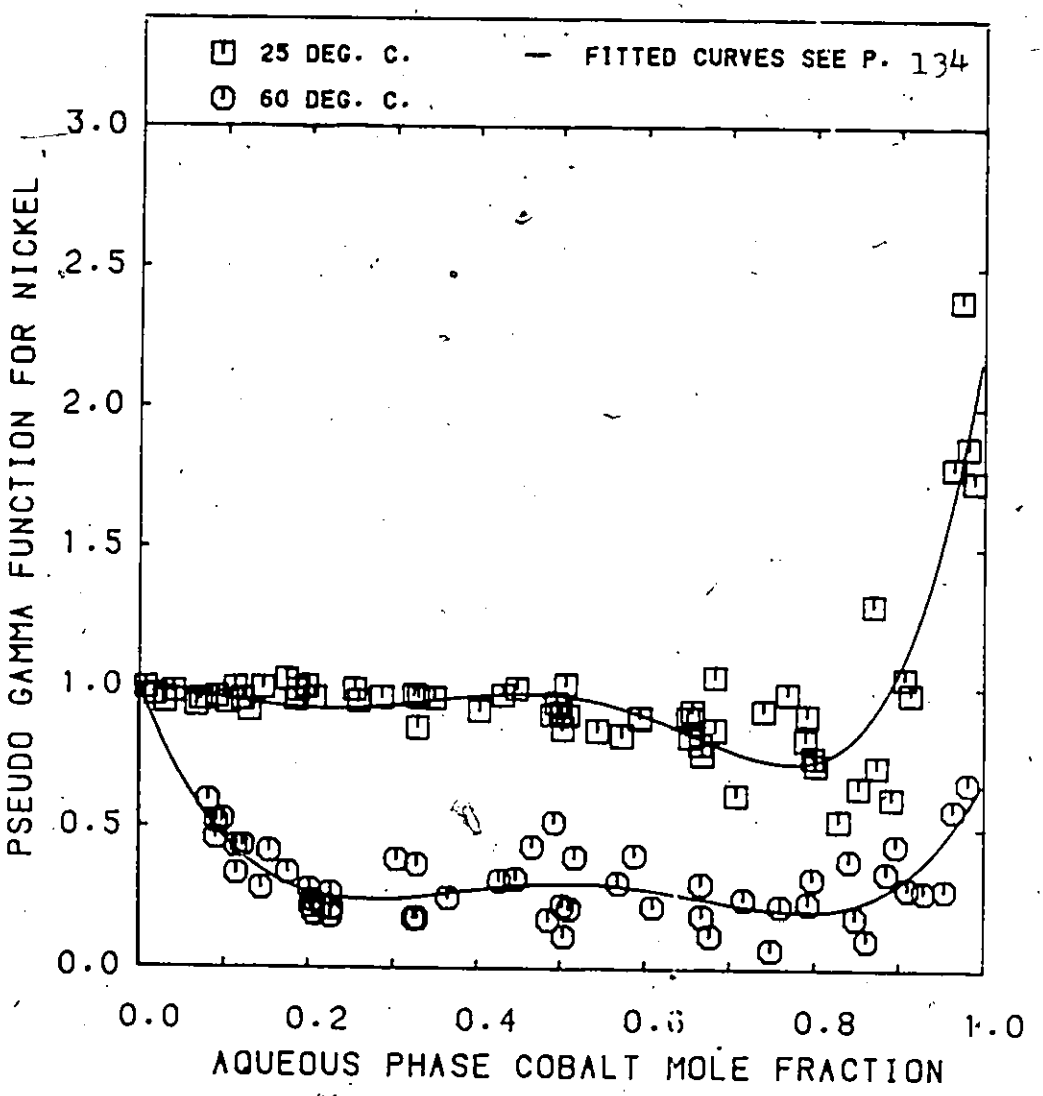


FIGURE 15. PSEUDO GAMMA FUNCTION FOR NICKEL

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH AT 25 DEG. C. = 5.3-6.4.
EQUILIBRIUM PH AT 60 DEG. C. = 5.5-6.4; A/O = 1.

From the definition of the PSEUDO GAMMA function it can be seen that at $x_i = 1.0$, γs_i becomes equal to one, while at $x_i = 0$, it is not clear what γs_i should be.

It was decided to correlate the PSEUDO GAMMA function by means of the mole fractions due to the fact that in vapour-liquid equilibrium the activity coefficients are usually correlated in this fashion. It was also easier to develop a model in which the limit for the PSEUDO GAMMA function approached 1.0 as the mole fraction approached 0 instead of 1.0. For this reason the the PSEUDO GAMMA function for component A was plotted as a function of the mole fraction (on a solvent free basis) of component B.

Figure 14 shows the PSEUDO GAMMA values for cobalt at 25 and 60 degrees Celsius as functions of the aqueous phase nickel mole fraction. The cobalt curves appear to follow a reasonably smooth pattern. The values of the PSEUDO GAMMA functions increase exponentially as the aqueous phase nickel mole fraction increases. Figure 15 shows the PSEUDO GAMMA functions for nickel at 25 and 60 degrees Celcius as functions of the aqueous phase cobalt mole fractions. These curves do not follow the smooth trends that the cobalt curves followed. For the nickel extraction at 25 degrees the PSEUDO GAMMA values are relatively constant at a value of 1.0 for $0 < x_{Co} < 0.6$. However at a cobalt mole fraction of about 0.7 there is a drop in the PSEUDO GAMMA curve followed by a relatively dramatic increase which occurs at a cobalt mole fraction of about 0.9. The PSEUDO GAMMA curve for nickel at 60 degrees Celcius shows a slightly parabolic type of a trend but the data has too much scatter in it to accurately describe this trend.

Due to the rather bizarre behaviour for the nickel functions a polynomial equation was used to fit the data since it would have been quite difficult to develop another type of equation which would have described the PSEUDO GAMMA functions for both metals at both temperatures. This equation is given below.

$$\gamma s_A = 1 + \alpha_1 x_B + \alpha_2 x_B^2 + \alpha_3 x_B^3 + \alpha_4 x_B^4 + \alpha_5 x_B^5 \qquad \ldots(28)$$

Due to the large scatter in the PSEUDO GAMMA functions for nickel it appeared that to correlate the data properly, some other "independent" variables may have been needed. The data appeared to show no easily definable trends as an explicit function of aqueous phase metal concentrations so these were left out of the simple polynomial model but it is quite likely that a more adequate model could have been constructed if the explicit aqueous phase metal concentrations were included in the model form.

The parameter estimates and information about the parameters can again be found in Appendix C. The confidence intervals for the parameter estimates seemed rather large but the large numbers of parameters were deemed necessary to reduce the residual trends as much as possible. The residual plots for the PSEUDO GAMMA values for cobalt at 25 degrees showed no apparent trends. For the PSEUDO GAMMA values for cobalt at 60 degrees Celsius the only trend in the residuals was found at high x_{Ni} values where there was significantly more scatter in the data. Again more data should be collected in this region. For the

nickel extraction at 25 degrees Celcius, there are definite sinusoidal trends in the PSEUDO GAMMA residual plots and heteroscedasticity is also evident. The residual plots for the PSEUDO GAMMA function for nickel at 60 degrees C show few trends but this is likely due to the fact that there is little correlation between the actual PSEUDO GAMMA function and the predicted PSEUDO GAMMA function (see Figure 15A2 in appendix F). This would tend to indicate that the model is incorrect, the data has just too much error associated with it and/or that this method is not suitable for predicting the organic phase nickel concentrations.

Before assessing the accuracy of the DELTA Y, the MOLE FRACTION, and the PSEUDO GAMMA methods for predicting organic phase compositions of cobalt and nickel a number of important trends should be discussed.

1. A number of plots show data that exhibit heteroscedasticity.
2. Some of the models appear to be inadequate at the end points.

These two trends may well be interrelated. While the inadequacies at the end points of some of the fitted models may be due to the forms of the models that were chosen they may also be due to errors in the data. From looking at the nature of the sodium correction factor (see Figures 28 and 29 in Appendix D) it can be seen that for both cobalt and nickel curves the correction factor that had to be used increased exponentially as the dilution factor decreased. It can also be seen that the magnitude of the required correction was quite significant at low dilution factors. These two factors lead to the conclusion that the errors associated with determining the equilibrium concentrations will

not be the same over all operating conditions and will be larger for samples which were measured with low dilution factors. This means that samples with low concentrations and usually either relatively low or relatively high mole fractions would be expected to have more error associated with them. This could account, at least in part, for both trends mentioned above.

4.8 Comparison of the DELTA Y, the MOLE FRACTION and the PSEUDO GAMMA Methods for Predicting Binary Equilibria

To evaluate and compare the overall ability of the three methods to predict organic phase metal concentrations from aqueous phase concentrations a number of criteria were utilized. Plots were made of the actual individual organic phase concentrations as a function of the predicted individual organic phase concentrations. The magnitude of the errors between the actual and predicted organic phase concentrations were tabulated in a number of different forms. The average error and the overall range of the errors were given. The percentage of the data points under 5 and 10 % error was also provided in these tables. Since these statistics may be misleading, plots were also made of the percent error as a function of both the aqueous phase metal concentration and the aqueous phase mole fractions. All these plots can be found in Appendix F.

While these methods of analyzing the results may not have been statistically rigourous they were simple and provided some basis for comparing the results. The statistical packages used for this thesis (see Appendix B) did not provide the 95 % confidence intervals for future

predictions for the types of models in question and due to the large number of equations that had to be analyzed a method to determine these confidence intervals was not implemented.

4.8.1 Cobalt at 25 degrees Celsius

For cobalt at 25 degrees Celcius, Figures 16, 17 and 18 show the actual organic phase cobalt concentration as a function of the predicted organic phase concentrations for the DELTA Y, the MOLE FRACTION and the PSEUDO GAMMA method respectively. From these figures alone it would appear that the MOLE FRACTION method would be the best followed by the DELTA Y and PSEUDO GAMMA methods. However, the % error curves (Figures 16A, 16B, 17A, 17B, 18A, and 18B in the Residual Appendix) show some rather interesting trends. The errors associated with the DELTA Y method appear relatively random as a function of x_{Co} but they show a definite trend as a function of the actual concentration, X'_{Co}. This suggested that the model that was fit to this DELTA Y function should be adjusted to place more emphasis on the actual concentration. The MOLE FRACTION method should be the most accurate since one extra piece of information was given, ie. the total metal concentration in the organic phase. From the % error vs. the aqueous compositions definite trends in the predictions can be seen. In both cases predicting organic phase cobalt concentrations at low aqueous phase cobalt concentrations and mole fractions gave large errors that consistently underestimated the concentration.

The PSEUDO GAMMA function had a larger % error than the MOLE FRACTION method but no trends were evident in the error as a function of the aqueous phase mole fraction and only slightly skewed results

for the error as a function the actual aqueous phase cobalt concentration were obtained. The magnitudes of the errors for each of these three methods can be seen from Table 1. The average error was less than 8 % in all cases while the MOLE FRACTION method had the lowest average error of about 4.8 %. The errors ranged from -36 % to as high as 23 %. The danger of quoting just the average errors can be clearly seen since if a prediction is made with any of the three methods the error in the prediction depends to a great degree on what the specific aqueous phase concentrations are.

4.8.2 Nickel at 25 degrees Celsius

All ACT. vs. PRED. curves for nickel at 25 degrees Celcius appear to show reasonably good fits (see Figures 19, 20 and 21). However from the % error curves some drastic trends can be seen. All 3 methods appear extremely accurate at high x_{Ni} and X'_{Ni} values (although some sinusoidal trends are evident). As these aqueous concentrations decrease, the magnitude of the % error increases dramatically. From Table 2 all the average errors for predicting the organic phase nickel concentrations are below 13 % with the lowest ayerage error being just under 10 % for the PSEUDO GAMMA method. This is an even more dramatic example of the location of a prediction affecting the accuracy of this prediction.

4.8.3 Cobalt at 60 degrees Celsius

Both the DELTA Y and PSEUDO GAMMA graphs of ACT. vs. PRED. show sinusoidal trends (see Figures 22 and 24) which are difficult to see from the % error curves . The Act. vs. Pred. curve for the MOLE

FRACTION method (Figure 23) does not exhibit these trends but it shows some heteroscedastic behaviour in the % error curves. From Table 3 the sizes of the errors can be seen and these magnitudes are quite small in comparison to all the other cases. In fact, aside from one or two data points, all the predictions were within 10 % and for each method more than 60 % of the data points were within 5 % of the actual organic phase cobalt concentration. The lowest average error was obtained with the PSEUDO GAMMA method. Once again, however, the trends in the results must be considered and the limited range of organic phase concentrations for which the models are valid should definitely be noted.

4.8.4 Nickel at 60 degrees Celsius

Figures 25, 26 and 27 all show the ACT. vs. PRED. plots for nickel at 60 degrees. It is evident that there is a great deal of scatter in these results. The error curve for the DELTA Y function was skewed similarly to the other skewed curves only the magnitudes of the errors were much larger. The MOLE FRACTION method % error curve showed that at low concentrations and mole fractions the predictions overestimated the results. There was an exponential decrease in error as concentration increased. While the % errors using the PSEUDO GAMMA method were lower than the other two methods, they still showed large inaccuracies and significant trends. The distribution of the % errors can be seen from Table 4. The average errors for nickel at 60 degrees Celcius for all of the methods was greater than 30 %. This was by far the worst set of results.

Attempts will now be made to explain some of these results. It would appear that the methods developed in this thesis were much more successful for predicting the organic phase cobalt concentration than for predicting the organic phase nickel concentration in a binary system of cobalt and nickel. It has already been mentioned that due to the affects of sodium on the absorbance of cobalt and nickel, a correction factor had to be applied. It is evident from Figures 28 and 29 in Appendix D that sodium affected the absorbance of nickel more than of cobalt. Most of the Atomic Absorption Spectrophotometer readings were taken with dilution factors between 800 and 5000. In this range the correction factor for nickel was 2 to 3 % higher than the cobalt correction factor. This may have had a significant effect on the precision of the results. Certainly, obtaining more accurate readings with the AAS is required. With the large effect that sodium has on the absorbance of both cobalt and nickel, it may be preferable to saturate the organic phase with ammonium hydroxide instead of sodium hydroxide. However, either a fresh solution of ammonium hydroxide would have to be used for each run, or some other method would have to be developed to ensure a constant saturation level was being attained.

Other sources of error that would lead to less accurate results for nickel than for cobalt were not apparent. The magnitudes of the absorbance readings for both cobalt and nickel were quite similar. During each measurement period with the AAS, standards of known concentration were run to check the accuracy of the calibration curves. In all cases these standards were within 5 % and usually within 3 % of their known concentrations and the errors in the nickel standards were not noticeably different from the errors in the cobalt standards.

Examining the DELTA Y method and the PSEUDO GAMMA method more closely (the MOLE FRACTION method is obviously quite limited) one can see the following areas which might contribute to the errors in the predictions of organic phase concentrations.

1. The actual methods (PSEUDO GAMMA and DELTA Y) themselves may not be suitable for predicting binary equilibrium.
2. The pure error variances may be too large to obtain satisfactory results with the number of data points that were used in the present study.
3. The error in modelling the pure component isotherms may be large enough that the actual trends in the PSEUDO GAMMA and DELTA Y functions may be hidden.
4. Some of the specific models that were used to fit the DELTA Y and PSEUDO GAMMA functions may not have been adequate enough to represent the data.

The first point might be a valid one but the only way this could be determined is if more data were collected, especially in the concentration ranges not studied in this present work and for the concentrations that showed peculiar trends (for example, the dip in the 25 degree Celcius PSEUDO GAMMA curve for nickel).

The second point is definitely responsible for some of the problems that were found in trying to develop these methods. Since the AAS gave errors usually between 2 and 5 % for known standards and since the quantity of sodium present in the aspirated samples affected the absorbances of both cobalt and nickel the measured concentrations could have been significantly different from the true concentrations. The

lack of a confirmed mass balance at low metal concentrations is another reason to be concerned with some of the results.

The third point can be seen more clearly since both the PSEUDO GAMMA method and the DELTA Y method involve correlating functions which can be viewed as correction factors which correct for deviations from "ideality". This is especially true of the DELTA Y function. If one looks at the DELTA Y curve for nickel at 25 degrees Celsius, the scatter in the data may well be due to the fact that this system is close to being "ideal" and therefore the magnitude of the DELTA Y function is quite small and of the same magnitude as the error associated with the pure component isotherm. The more "non-ideal" the system, the greater the chance that the error associated with the pure component isotherm will be insignificant in comparison to the DELTA Y or PSEUDO GAMMA function. This is good in so far as developing appropriate models is concerned because the better, more commercially promising extractants should behave more "non-ideally" than the poorer ones.

The final point is definitely valid for some of the models that were fit in this thesis. It is obvious that with more ingenuity, better models could have been developed. The inclusion of both the aqueous phase mole fractions and the explicit concentrations appears to be required for appropriate descriptions of the extraction process. The actual extraction process is obviously too complex to develop mechanistic models at the present time, and, while there are a number of other factors that can be used to correlate the organic phase concentrations the use of just the aqueous concentrations and mole fractions would make these methods easily applicable to other liquid-liquid extraction systems.

Many of the modelling problems like heteroscedasticity are not just restricted to liquid-liquid extraction equilibria. The same problems can also be found in vapour-liquid equilibria. The proper methods of dealing with these problems should be investigated more thoroughly and implemented where possible.

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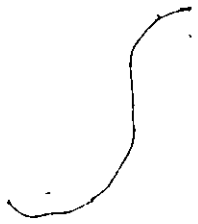
Chapter V

CONCLUSIONS

1. For correlating liquid-liquid binary equilibria the use of an approach in which organic and aqueous phase concentrations of one metal are plotted as functions of the aqueous phase concentration of the other metal will not be amenable, in practical situations, to a McCabe-Thiele approach for determining the number of ideal extraction stages that would be required for a given separation.
2. DELTA Y and PSEUDO GAMMA methods can be used to predict to within a reasonable degree of error the organic phase cobalt concentrations in a binary system of cobalt and nickel.
3. The DELTA Y and PSEUDO GAMMA methods are much less accurate for predicting the organic phase nickel concentrations in a binary system of cobalt and nickel.
4. The modelling of the DELTA Y function can be more easily performed for more "non-ideal" systems.
5. The models used to predict organic phase concentration require more than just the aqueous phase mole fractions to adequately describe the data. These models appear to require a more explicit form of the concentration.
6. The MOLE FRACTION method may not be suitable to directly model the equilibrium data. In the unlikely event that it is suit-

able, the total organic phase metal concentration or some other piece of information would be required to predict the individual organic phase concentrations.



Chapter VI

RECOMMENDATIONS

1. The problems associated with the analysis of the metal concentrations must be addressed and overcome before more concrete conclusions can be made regarding the proposed methods. The adoption of ammonia for the pre-equilibration process would be a reasonable step to take as long as methods were developed to ensure a constant saturation level was maintained.
2. The methods discussed in this thesis should be used with other metal-extractant systems to see if these methods would be suitable for describing more than just the extraction of cobalt and nickel with D2EHPA.
3. If it is found that other binary liquid-liquid extraction systems aside from the Co/Ni-D2EHPA system can be described by these methods, then general model forms which adequately describe the PSEUDO GAMMA and DELTA Y functions for all the different systems should be developed.
4. The method of collecting the data in this thesis was extremely time consuming, and since the form of the data was required only for the McCabe-Thiele approach which could not be used for systems of practical importance, this method of collecting data should be discontinued. Data should be obtained for a wide range of total organic phase loadings and ratios of cobalt to nickel in the aqueous and the organic phases.

5. For extractants that show relatively different selectivities for a metal at different temperatures, the temperature effect could be incorporated into the modelling process.

6. It would appear that unless extremely large strides are made in understanding the chemistry of solvent extraction processes, the use of empirical methods will be required to represent binary equilibria and further analogies to vapour-liquid equilibrium and adsorption may prove useful.

Chapter VII

TABLES

Table 1: ERRORS IN THE PREDICTIONS OF THE ORGANIC PHASE COBALT CONCENTRATION AT 25 DEGREES CELSIUS

DELTA Y METHOD		MOLE FRACTION METHOD		PSEUDO GAMMA METHOD	
% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR	% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR	% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR
37.7	75.4	73.4	83.6	37.7	67.2
RANGE OF % ERROR		RANGE OF % ERROR		RANGE OF % ERROR	
-34 TO 23		-28 TO 15		-16 TO 23	
AVERAGE % ERROR		AVERAGE % ERROR		AVERAGE % ERROR	
8.0		4.8		7.8	

Table 2: ERRORS IN THE PREDICTIONS OF THE ORGANIC PHASE NICKEL CONCENTRATION AT 25 DEGREES CELSIUS

DELTA Y METHOD		MOLE FRACTION METHOD		PSEUDO GAMMA METHOD	
% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR	% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR	% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR
52.5	68.9	63.9	68.9	42.6	72.1
RANGE OF % ERROR		RANGE OF % ERROR		RANGE OF % ERROR	
-72 TO 62		-66 TO 62		-33 TO 66	
AVERAGE % ERROR		AVERAGE % ERROR		AVERAGE % ERROR	
12.9		11.2		9.9	

Table 3: ERRORS IN THE PREDICTIONS OF THE ORGANIC PHASE COBALT CONCENTRATION AT 60 DEGREES CELSIUS

DELTA Y METHOD		MOLE FRACTION METHOD		PSEUDO GAMMA METHOD	
% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR	% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR	% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR
67.3	96.2	69.2	96.2	75.0	94.2
RANGE OF % ERROR		RANGE OF % ERROR		RANGE OF % ERROR	
-12 TO 21		-11 TO 12		-14 TO 10	
AVERAGE % ERROR		AVERAGE % ERROR		AVERAGE % ERROR	
4.5		3.8		3.5	

Table 4: ERRORS IN THE PREDICTIONS OF THE ORGANIC PHASE NICKEL CONCENTRATION AT 60 DEGREES CELSIUS

DELTA Y METHOD		MOLE FRACTION METHOD		PSEUDO GAMMA METHOD	
% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR	% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR	% OF DATA POINTS UNDER 5 % ERROR	% OF DATA POINTS UNDER 10 % ERROR
9.6	21.2	5.8	25.0	7.7	19.2
RANGE OF % ERROR		RANGE OF % ERROR		RANGE OF % ERROR	
-172 TO 89		-41 TO 412		-43 TO 215	
AVERAGE % ERROR		AVERAGE % ERROR		AVERAGE % ERROR	
33.0		43.2		33.5	

Appendix A

EXPERIMENTAL EQUIPMENT

pH values for all aqueous phase samples were determined with an ORION RESEARCH DIGITAL IONALYZER/501. An ORION 91-05 combination pH electrode was used for each measurement. The constant temperature "shaking water bath" model 127 was made by Fisher.

Metal concentrations were determined with a Fisher Jarrel-Ash Dial Atom III Atomic Absorption Spectrophotometer (AAS). This instrument uses an oxygen-acetylene flame to burn a sample whose metal concentration is to be determined. If the metals are bound to other atoms or molecules the thermal and chemical reactions in the flame cause the sample to break down into free atoms which can absorb or emit light of a specific wavelength. The AAS has two main modes of operation, flame emission and atomic absorption. The use of each mode is governed by the particular metal whose concentration is to be determined. The determination of cobalt, nickel and sodium concentrations was carried out in the absorption mode. In this mode, a hollow cathode lamp corresponding to the particular metal to be determined, is used to produce a band of narrow spectral lines associated with this metal. A monochromator isolates and determines the intensity of this band of wavelengths. Thus, when metal atoms absorb light of a specific wavelength the monochromator will measure light of a lower intensity coming from the

hollow cathode lamp. This decrease in intensity is related to the amount of light absorbed which is related to the concentration of metal present. It has been found that for certain concentration ranges absorbance is linearly dependent on the concentration. A calibration curve can then be drawn after determining the absorbance of standards of known concentration. The suggested operating conditions for determining the concentrations of the particular metals of interest are given below.

element	current (mA)	slit size (micron)	operating range (ppm)
cobalt	12	50	1-10
nickel	8	50	2-12
sodium	8	50	0.1-1.0

Appendix B

STATISTICAL ANALYSIS AND CURVE FITTING PROCEDURES

B.1 Sample Curve Fitting Program

SAS software was used for all the curve fitting and data analysis in this thesis. The following program is a sample SAS program which was used to curve fit the mole fraction data obtained at 25 degrees Celsius. The program lines are indented while the comments begin with COM. and follow each program line.

```
    DATA FIRST ;
```

COM. This line tells SAS to begin a Data step and to start building a SAS data set.

```
    TITLE MOLE FRACTION METHOD AT 25 DEG. C.;
```

COM. This is the title which will appear at the top of each page of the listing file.

```
    CMS FILEDEF HWDATA DISK MOO25 DATA A ;
```

COM. This line tells SAS that the data is in the external CMS file called MOO25 DATA stored on an A disk.

```
    INFILE HWDATA ;
    INPUT X2 2-8 Y2 10-16 A2 19-24 O2 27-32 X1 34-40 Y1 43-48 ;
```

```
COM. These lines provide the locations and the names of the variables
on the CMS data set.
     PROC PRINT ;
COM. This line prints the input data.
     PROC NLIN BEST=10 PLOT METHOD=MARQUARDT ;
COM. This line accesses the SAS nonlinear regression package and spec-
ifies the use of the Marquardt procedure for the convergence routine.
     PARMS B=-1.45 C=1.0 ;
COM. This line provides the initial parameter estimates.
     NE=(1-A2)**C+A2 ;
     MODEL O2=(A2+B*(A2**2-A2))/NE  ;
COM.  These lines define the proposed model.
     DER.B=(A2**2-A2)/NE ;
     DER.C=(A2+B*(A2**2-A2))*(-LOG(1-A2)*(NE-A2))/(NE**2) ;
COM. These lines provide the partial derivatives of the model with
respect to the parameters.
     OUTPUT OUT=B P=PRED R=RESID ;
COM. This line creates an output SAS data set called B which contains
the regression results as well as predicted and residual values.
     PROC PLOT DATA=B ;
     PLOT O2*A2='A' PRED*A2='P' / OVERLAY VPOS=50 ;
     PLOT RESID*A2 / VREF=0 OVERLAY VPOS=50 ;
     PLOT RESID*PRED / VREF=0 OVERLAY VPOS=50 ;
COM. These lines plot the various x-y, and residual graphs that will be
of use in the model analysis.
     PROC PRINT R ;
```

COM. This line creates a table at the end of the output file which contains the input data as well as the predicted and residual values.

B.2 Linear Curve Fitting Procedures

For some of the models that were linear in the parameters (for example the AAS calibration curves) the "PROC REG" SAS procedure was used for the regression analysis. The procedures used by SAS will be outlined below.

A linear model can be represented by equation (29)

$$\underline{Y} = \underline{X}\,\underline{\beta} + \underline{\varepsilon} \qquad \ldots(29)$$

where matrices are denoted by an underscore, $\underline{Y}$ is a vector of response (dependent) variables, $\underline{X}$ is a matrix containing the values of the independent variables, $\underline{\beta}$ is a vector of parameters and $\underline{\varepsilon}$ is a vector of unknown random errors. Now $\underline{e}$ is a vector of residuals such that

$$\underline{e} = \underline{Y} - \underline{X}\,\underline{\tilde{\beta}} \qquad \ldots(30)$$

where the $\sim$ denotes any given value for the parameter. The SAS procedure obtains the least squares estimates of the parameters by minimizing $\underline{e}^T\underline{e}$. This is done by solving the set of normal equations (ie. the set of equations in which the partial derivatives of $\underline{e}^T\underline{e}$ with respect to the parameters are set equal to zero). This leads to the following expression for the parameter estimates.

$$\hat{\underline{\beta}} = (\underline{X}^T\underline{X})^{-1}\ \underline{X}^T\ \underline{Y} \qquad \ldots(31)$$

where the superscript T denotes the transpose of a matrix and the superscript -1 denotes the inverse of a matrix.

The SAS procedures also give a number of other useful pieces of information which will be outlined below. While all of these procedures were available for certain types of linear model procedures in SAS, only a few were available for the nonlinear procedures.

The correlation matrix for the parameter estimates (CORRB) is found from the following equation.

$$\text{CORRB} = \underline{S}(\underline{X}^T\ \underline{X})^{-1}\ \underline{S} \qquad \ldots(32)$$

where $\underline{S} = \text{diag}((\underline{X}^T\ \underline{X})^{-1})^{-0.5}$. The correlations between parameter estimates range between -1 and 1. The closer the correlation is to 1 or -1 the higher the correlation is between parameter estimates. Ideally one would want no correlation between parameter estimates but this is rarely achieved in practice.

Most SAS procedures provide estimates of parameter precision by providing individual $100(1-\alpha)$ per cent confidence intervals for the parameter estimates according to the following equation.

$$\hat{\beta}_i \pm t_{\nu,\alpha/2}(\text{estimated variance of } \hat{\beta}_i)^{0.5} \qquad \ldots(33)$$

where the t term is the upper $\alpha/2$ per cent value of the t_v distribution, v is the number of degrees of freedom associated with an estimate of pure error variance and the estimated variance of $\hat{\beta}_i$ is the diagonal element in the variance-covariance matrix which is given by

$$COVB = (\underline{X}^T\underline{X})^{-1}\hat{\sigma}^2 \qquad \ldots(34)$$

where $\hat{\sigma}^2$ is an estimate of the pure error variance.

Some SAS procedures provide estimates of the precision for future predictions of individual response values y_k^f. A $100(1-\alpha)$ per cent confidence interval for a future prediction of a response value is given by the following equation.

$$\hat{y}_k \pm t_{v,\alpha/2}(\text{estimated variance of } y_k^f)^{0.5} \qquad \ldots(35)$$

where the t term is the upper $\alpha/2$ per cent value of the t_v distribution, v is the number of degrees of freedom associated with an estimate of pure error variance and the estimated variance of y_k^f is dependent on the actual values of the operating conditions.

The next section will briefly discuss some of the differences in estimating parameters for nonlinear (in the parameters) models.

B.3 Nonlinear Curve Fitting Procedures

The application of the least squares criterion is also used by SAS for fitting nonlinear models. However, using a least squares analysis for nonlinear models does not necessarily produce estimates that are unbiased and these estimates do not necessarily have minimum variance. These properties are only asymptotically approached as the number of data points increase. For nonlinear models the set of normal equations contains at least one nonlinear normal equation. Parameter values cannot, therefore, be directly determined as in the linear least squares case. A number of iterative schemes have been proposed to converge to the least squares estimates. The Marquardt method was the one chosen to perform this function for the nonlinear equations in this thesis.

Consider the following general nonlinear equation

$$\underline{Y} = \underline{F}(\underline{\beta}, \underline{\xi}) + \underline{\varepsilon} \qquad \ldots(36)$$

where the ξ's are the independent variables. For $\underline{X} = \partial \underline{F} / \partial \underline{\beta}$ the Marquardt procedure uses an iterative approach from the initial parameter estimates, $\underline{X}$ and $\underline{Y}$ to compute $\underline{\Delta}$ such that.

$$\text{SSE(parameter estimate} + \underline{k\Delta}) < \text{SSE(parameter estimate)} \qquad \ldots(37)$$

For Marquardt's method

$\underline{\Delta} = (\underline{X}^T\underline{X} + \lambda \underline{I})^{-1} (\underline{X}^T\underline{e})$, $\underline{k}$ is a vector of step sizes, λ is a constant that adjusts the direction of convergence and $\underline{I}$ is the identity matrix. Marquardt's method is a combination of the steepest descent and the Gauss-Newton methods. It is especially useful for converging in situations where there are high correlations between parameter estimates. For estimating the individual parameter and future response confidence intervals the same procedures are used as in the linear case but for a variety of reasons these are only approximate.

Appendix C

EQUATION FORMS AND PARAMETER ESTIMATES

In the following tables U95 and L95 are the upper and lower individual 95 % confidence levels for the parameter estimates respectively. (For nonlinear models the confidence levels are only asymptotically valid.) SSR is the sum of squares of the residuals.

Table 5: PURE COMPONENT COBALT ISOTHERM AT 25 DEGREES CELSIUS

$Y' = \theta_1\theta_2X' / (1+\theta_2X') + \theta_3X'^{\theta_4}$

COBALT

PARAMETER ESTIMATES		L95	U95
θ_1	+4.520	1.8	7.3
θ_2	+1.0 (set)	1.0	1.0
θ_3	+6.522	5.2	7.8
θ_4	+0.1284	0.090	0.17

CORRELATIONS

$\theta_1\theta_3$	-0.963
$\theta_1\theta_4$	-0.847
$\theta_3\theta_4$	+0.696

SSR 10.7

Table 6: PURE COMPONENT NICKEL ISOTHERM AT 25 DEGREES CELSIUS

$Y' = \theta_1\theta_2X' / (1+\theta_2X') + \theta_3X'^{\theta_4}$

NICKEL

PARAMETER ESTIMATES		L95	U95
θ_1	+3.025	0.59	5.5
θ_2	+1.0 (set)	1.0	1.0
θ_3	+6.991	5.8	8.2
θ_4	+0.1468	0.12	0.17

CORRELATIONS

$\theta_1\theta_3$	-0.961
$\theta_1\theta_4$	-0.752
$\theta_3\theta_4$	+0.563

SSR 5.13

Table 7: PURE COMPONENT COBALT ISOTHERM AT 60 DEGREES CELSIUS

$Y' = \theta_1\theta_2X' / (1+\theta_2X') + \theta_3X'^{\theta_4}$

COBALT

PARAMETER ESTIMATES	L95	U95
θ_1 +14.82	14.1	15.5
θ_2 +27.82	22.2	33.5
θ_3 +0.08073	0.04	0.12
θ_4 +1.0 (set)	1.0	1.0

CORRELATIONS

$\theta_1\theta_2$	-0.629
$\theta_1\theta_3$	-0.837
$\theta_2\theta_3$	+0.520

SSR 11.56

Table 8: PURE COMPONENT NICKEL ISOTHERM AT 60 DEGREES CELSIUS

$Y' = \theta_1\theta_2X' / (1+\theta_2X') + \theta_3X'^{\theta_4}$

NICKEL

PARAMETER ESTIMATES		L95	U95
θ_1	+9.205	8.8	9.6
θ_2	+11.54	8.9	14.
θ_3	+1.0 (set)	1.0	1.0
θ_4	+0.5719	0.54	0.60

CORRELATIONS

$\theta_1\theta_2$	-0.679
$\theta_1\theta_4$	-0.868
$\theta_2\theta_4$	+0.581

SSR 1.59

Table 9: BINARY COMPONENT COBALT ISOTHERM AT 25 DEGREES CELSIUS WITH 3 G/L OF NICKEL IN THE AQUEOUS PHASE

$Y' = \theta_1\theta_2X' / (1+\theta_2X')$

COBALT

PARAMETER ESTIMATES		L95	U95
θ_1	+18.39	16.	21.
θ_2	+0.1950	0.13	0.26

CORRELATIONS

$\theta_1\theta_2$	-0.877
SSR	3.81

Table 10: BINARY COMPONENT NICKEL ISOTHERM AT 25 DEGREES CELSIUS WITH 3 G/L OF COBALT IN THE AQUEOUS PHASE

$Y' = \theta_1\theta_2X' / (1+\theta_2X')$

NICKEL

PARAMETER ESTIMATES		L95	U95
θ_1	+15.83	15.3	16.3
θ_2	+0.1436	0.13	0.16

CORRELATIONS

$\theta_1\theta_2$	-0.904
SSR	0.207

Table 11: BINARY COMPONENT COBALT ISOTHERM AT 25 DEGREES CELSIUS WITH 6 G/L OF NICKEL IN THE AQUEOUS PHASE

$Y' = \theta_3 X' \cdot \theta_4$

COBALT

PARAMETER ESTIMATES		L95	U95
θ_3	+2.757	2.3	3.2
θ_4	+0.5260	0.47	0.59

CORRELATIONS

$\theta_3\theta_4$	-0.982
SSR	1.40

Table 12: BINARY COMPONENT NICKEL ISOTHERM AT 25 DEGREES CELSIUS WITH 6 G/L OF COBALT IN THE AQUEOUS PHASE

$Y' = \theta_1\theta_2 X' / (1+\theta_2 X')$

NICKEL

PARAMETER ESTIMATES		L95	U95
θ_1	+17.43	16.0	18.8
θ_2	+0.07820	0.063	0.93

CORRELATIONS

$\theta_1\theta_2$	-0.958
SSR	0.265

Table 13: BINARY COMPONENT COBALT ISOTHERM AT 25 DEGREES CELSIUS WITH 12 G/L OF NICKEL IN THE AQUEOUS PHASE

$Y' = \theta_3 X'^{\theta_4}$

COBALT

PARAMETER ESTIMATES		L95	U95
θ_3	+1.698	1.5	1.9
θ_4	+0.6328	0.59	0.68

CORRELATIONS

$\theta_3\theta_4$	-0.988
SSR	0.45

Table 14: BINARY COMPONENT NICKEL ISOTHERM AT 25 DEGREES CELSIUS WITH 12 G/L OF COBALT IN THE AQUEOUS PHASE

$Y' = \theta_1\theta_2 X' / (1+\theta_2 X')$

NICKEL

PARAMETER ESTIMATES		L95	U95
θ_1	+20.10	16.2	24.0
θ_2	+0.03075	0.021	0.040

CORRELATIONS

$\theta_1\theta_2$	+0.984
SSR	0.58

Table 15: BINARY COMPONENT COBALT ISOTHERM AT 25 DEGREES CELSIUS WITH 24 G/L OF NICKEL IN THE AQUEOUS PHASE

$Y' = \theta_3 X'^{\theta_4}$

COBALT

PARAMETER ESTIMATES		L95	U95
θ_3	+1.698	1.5	1.9
θ_4	+1.021	0.91	1.1

CORRELATIONS

$\theta_3\theta_4$	-0.977
SSR	0.390

Table 16: BINARY COMPONENT NICKEL ISOTHERM AT 25 DEGREES CELSIUS WITH 24 G/L OF COBALT IN THE AQUEOUS PHASE

$Y' = \theta_3 X'^{\theta_4}$

NICKEL

PARAMETER ESTIMATES		L95	U95
θ_3	+0.3375	0.20	0.47
θ_4	+0.9351	0.81	1.1

CORRELATIONS

$\theta_3\theta_4$	-0.991
SSR	0.715

Table 17: THE DELTA Y FUNCTION FOR COBALT AT 25 DEGREES CELSIUS

$$\Delta Y_A = \beta_1(1-x_A)^{\beta_2} x_A^{\beta_3} X'^{\beta_4}_B + \beta_5(1-x_A)x_A X'^{\beta_6}_B$$

COBALT

PARAMETER ESTIMATES		L95	U95
β_1	-1.244	-1.41	-1.08
β_2	+1.237	+1.16	+1.32
β_3	+1.088	+1.02	+1.16
β_4	0.0 (set)	0.0	0.0
β_5	1.0 (set)	1.0	1.0
β_6	+0.05391	+0.036	+0.072

CORRELATIONS

$\beta_1\beta_2$	-0.926
$\beta_1\beta_3$	-0.838
$\beta_1\beta_6$	-0.483
$\beta_2\beta_3$	+0.838
$\beta_2\beta_6$	+0.235
$\beta_3\beta_6$	+0.010
SSR	0.00769

Table 18: THE DELTA Y FUNCTION FOR NICKEL AT 25 DEGREES CELSIUS

$$\Delta Y_A = \beta_1(1-x_A)^{\beta_2} x_A^{\beta_3} X_B^{\beta_4} + \beta_5(1-x_A)x_A X_B^{\beta_6}$$

NICKEL

PARAMETER ESTIMATES		L95	U95
β_1	-0.03500	-0.050	-0.020
β_2	+0.7878	+0.40	+1.2
β_3	1.0 (set)	1.0	1.0
β_4	0.0 (set)	0.0	0.0
β_5	0.0 (set)	0.0	0.0
β_6	0.0 (set)	0.0	0.0

CORRELATIONS

$\beta_1\beta_2$ -0.841

SSR 0.00246

Table 19: THE DELTA Y FUNCTION FOR COBALT AT 60 DEGREES CELSIUS

$$\Delta Y_A = \beta_1(1-x_A)^{\beta_2} x_A^{\beta_3} X_B^{\beta_4} + \beta_5(1-x_A)x_A X_B^{\beta_6}$$

COBALT

PARAMETER ESTIMATES		L95	U95
β_1	+0.3042	+0.22	+0.38
β_2	+1.028	+0.84	+1.2
β_3	+0.3656	+0.26	+0.47
β_4	+0.0739	0.027	0.12
β_5	0.0 (set)	0.0	0.0
β_6	0.0 (set)	0.0	0.0

CORRELATIONS

$\beta_1\beta_2$	+0.882
$\beta_1\beta_3$	0.829
$\beta_1\beta_4$	-0.567
$\beta_2\beta_3$	+0.857
$\beta_2\beta_4$	-0.231
SSR	0.00999

Table 20: THE DELTA Y FUNCTION FOR NICKEL AT 60 DEGREES CELSIUS

$$\Delta Y_A = \beta_1(1-x_A)^{\beta_2} x_A^{\beta_3} X_B^{\beta_4} + \beta_5(1-x_A)x_A X_B^{\beta_6}$$

NICKEL

PARAMETER ESTIMATES		L95	U95
β_1	-1.020	-1.095	-0.944
β_2	+0.6457	+0.60	+0.69
β_3	+0.9637	+0.91	+1.02
β_4	0.0 (set)	0.0	0.0
β_5	1.0 (set)	1.0	1.0
β_6	0.0 (set)	0.0	0.0

CORRELATIONS

$\beta_1\beta_2$	-0.958
$\beta_1\beta_3$	-0.938
$\beta_2\beta_3$	+0.852

SSR 0.00668

Table 21: MOLE FRACTION MODEL FOR COBALT AT 25 DEGREES CELSIUS

$$y_{Co} = (x_{Co} + \lambda_1(x_{Co}^2 - x_{Co})) / (x_{Co} + (1-x_{Co})^{\lambda_2})$$

COBALT

PARAMETER ESTIMATES		L95	U95
λ_1	-0.3145	-0.39	-0.24
λ_2	+1.103	1.0	1.2

CORRELATIONS

$\lambda_1\lambda_2$	+0.903
SSR	0.028

Table 22: MOLE FRACTION MODEL FOR COBALT AT 60 DEGREES CELSIUS

$$y_{Co} = (x_{Co} + \lambda_1(x_{Co}^2 - x_{Co})) / (x_{Co} + (1-x_{Co})^{\lambda_2})$$

COBALT

PARAMETER ESTIMATES		L95	U95
λ_1	+0.2188	+0.20	+0.24
λ_2	+32.80	30.8	34.8

CORRELATIONS

$\lambda_1\lambda_2$	+0.508
SSR	0.078

Table 23: THE PSEUDO GAMMA FUNCTION FOR COBALT AT 25 DEGREES CELSIUS

$$\gamma s_A = 1 + \alpha_1 x_B + \alpha_2 x_B^2 + \alpha_3 x_B^3 + \alpha_4 x_B^4 + \alpha_5 x_B^5$$

COBALT

PARAMETER ESTIMATES		L95	U95
α_1	+4.796	2.0	7.5
α_2	-38.04	-61.	-15.
α_3	+123.3	+58.	+190.
α_4	-166.0	-240.	-90.
α_5	+78.91	+50.	+110.

CORRELATIONS

$\alpha_1\alpha_2$	-0.970
$\alpha_1\alpha_3$	+0.922
$\alpha_1\alpha_4$	-0.875
$\alpha_1\alpha_5$	+0.833
$\alpha_2\alpha_3$	-0.987
$\alpha_2\alpha_4$	+0.961
$\alpha_2\alpha_5$	-0.932
$\alpha_3\alpha_4$	-0.993
$\alpha_3\alpha_5$	+0.977
$\alpha_4\alpha_5$	-0.995
SSR	1.68

Table 24: THE PSEUDO GAMMA FUNCTION FOR COBALT AT 60 DEGREES CELSIUS

$$\gamma s_A = 1 + \alpha_1 x_B + \alpha_2 x_B^2 + \alpha_3 x_B^3 + \alpha_4 x_B^4 + \alpha_5 x_B^5$$

COBALT

PARAMETER ESTIMATES		L95	U95
α_1	0.0 (set)	0.0	0.0
α_2	+10.44	+7.3	+14.
α_3	-24.28	-33.	-15.
α_4	+22.40	+16.	+29.
α_5	0.0 (set)	0.0	0.0

CORRELATIONS

$\alpha_2\alpha_3$	-0.987
$\alpha_2\alpha_4$	+0.961
$\alpha_3\alpha_4$	-0.993
SSR	1.90

Table 25: THE PSEUDO GAMMA FUNCTION FOR NICKEL AT 25 DEGREES CELSIUS

$$\gamma s_A = 1 + \alpha_1 x_B + \alpha_2 x_B^2 + \alpha_3 x_B^3 + \alpha_4 x_B^4 + \alpha_5 x_B^5$$

NICKEL

PARAMETER ESTIMATES		L95	U95
α_1	0.0 (set)	0.0	0.0
α_2	-7.334	-12.	-2.4
α_3	+38.92	+17.	+61.
α_4	-67.72	-100.	-36.
α_5	+37.37	+22.	+52.

CORRELATIONS

$\alpha_2\alpha_3$	-0.986
$\alpha_2\alpha_4$	+0.957
$\alpha_2\alpha_5$	-0.924
$\alpha_3\alpha_4$	-0.992
$\alpha_3\alpha_5$	+0.974
$\alpha_4\alpha_5$	-0.995

SSR 1.25

Table 26: THE PSEUDO GAMMA FUNCTION FOR NICKEL AT 60 DEGREES CELSIUS

$$\gamma s_A = 1 + \alpha_1 x_B + \alpha_2 x_B^2 + \alpha_3 x_B^3 + \alpha_4 x_B^4 + \alpha_5 x_B^5$$

NICKEL

PARAMETER ESTIMATES		L95	U95
α_1	-7.627	-8.4	-6.8
α_2	+26.57	+22.	+31.
α_3	-37.20	-45.	-29.
α_4	+17.94	+14.	+22.
α_5	0.0 (set)	0.0	0.0

CORRELATIONS

$\alpha_1\alpha_2$	-0.959
$\alpha_1\alpha_3$	+0.898
$\alpha_1\alpha_4$	-0.842
$\alpha_2\alpha_3$	-0.984
$\alpha_2\alpha_4$	+0.953
$\alpha_3\alpha_4$	-0.992
SSR	0.434

Appendix D

SAMPLE CALCULATIONS AND ERROR ANALYSIS

A sample calculation will be performed with one of the data points from Table 35. The equilibrium concentrations are given in table 27 along with some required information about this particular run.

Table 27: IMPORTANT INFORMATION FOR THE SAMPLE CALCULATION

X'_{Co}	=	5.81 g/l
Y'_{Co}	=	10.4 g/l
pH	=	5.98
X'_{Ni}	=	0.874 g/l
Y'_{Ni}	=	1.45 g/l
DF_{Co}	=	1600.
DF_{Ni}	=	200.
ABS_{Co}	=	133.4
ABS_{Ni}	=	128.6
$[Co]_f$	=	16.1846 g/l
$[Ni]_f$	=	2.3267 g/l
MW_{Co}	=	58.933 g/gmol
MW_{Ni}	=	58.71 g/gmol

Metal concentrations were obtained using an Atomic Absorption Spectrophotometer (AAS). Calibration curves were made by measuring the absorbance of standards of known concentrations and then plotting absorbance vs. metal concentration in ppm.

Since the amount of sodium transferred from the pre-equilibrated organic phase to the aqueous phase affected the absorbance of both cobalt and nickel a correction factor was applied to the absorbance readings. It was found that a relatively constant equilibrium aqueous phase sodium concentration was obtained even for relatively different total organic phase metal (Co and/or Ni) concentrations. This was due to the displacement of sodium by both the desired metals (cobalt and/or nickel) and the hydrogen ions. This movement of hydrogen atoms from the aqueous phase to the organic phase resulted in the increase in pH during the extraction process. It was found that the aqueous phase sodium concentration at equilibrium was 8.5 g/l (std. dev. 1.2 from 70 readings). Knowing this concentration and the dilution factors corresponding to a given measured absorbance of cobalt or nickel the sodium concentration in the AAS sample could be estimated. A correlation could therefore be made between the affect of sodium on the absorbance of cobalt or nickel and the dilution factor (indirectly the concentration). This might be seen more clearly by noting that a dilution factor (DF) of 800 corresponded to a sodium concentration of 8.5 g/l X 1000 ppm/(g/l) / 800 = 10.6 ppm .

Sodium standards were made with concentrations corresponding to dilution factors between 10 and 10000. Each of these standards had a cobalt or nickel concentration of 3.5 ppm. The absorbances of these standards were compared to the absorbance of a 3.5 ppm cobalt or nickel standard in which no sodium was present. The % difference (PER) between these absorbance readings was determined and then plotted against dilution factor. These figures can be found on the next few pages.

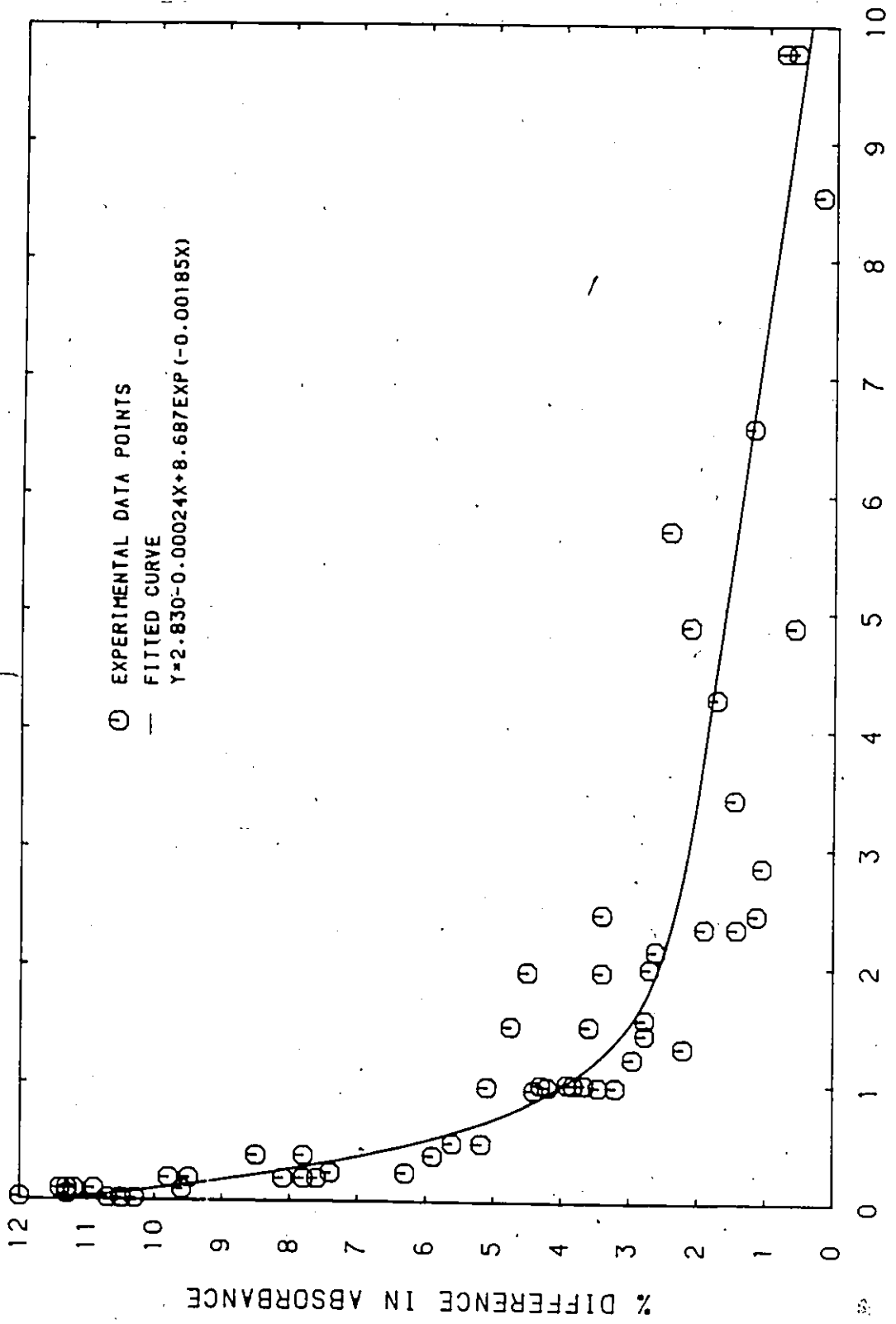


FIGURE 28. SODIUM CORRECTION FACTOR FOR THE ABSORBANCE OF COBALT

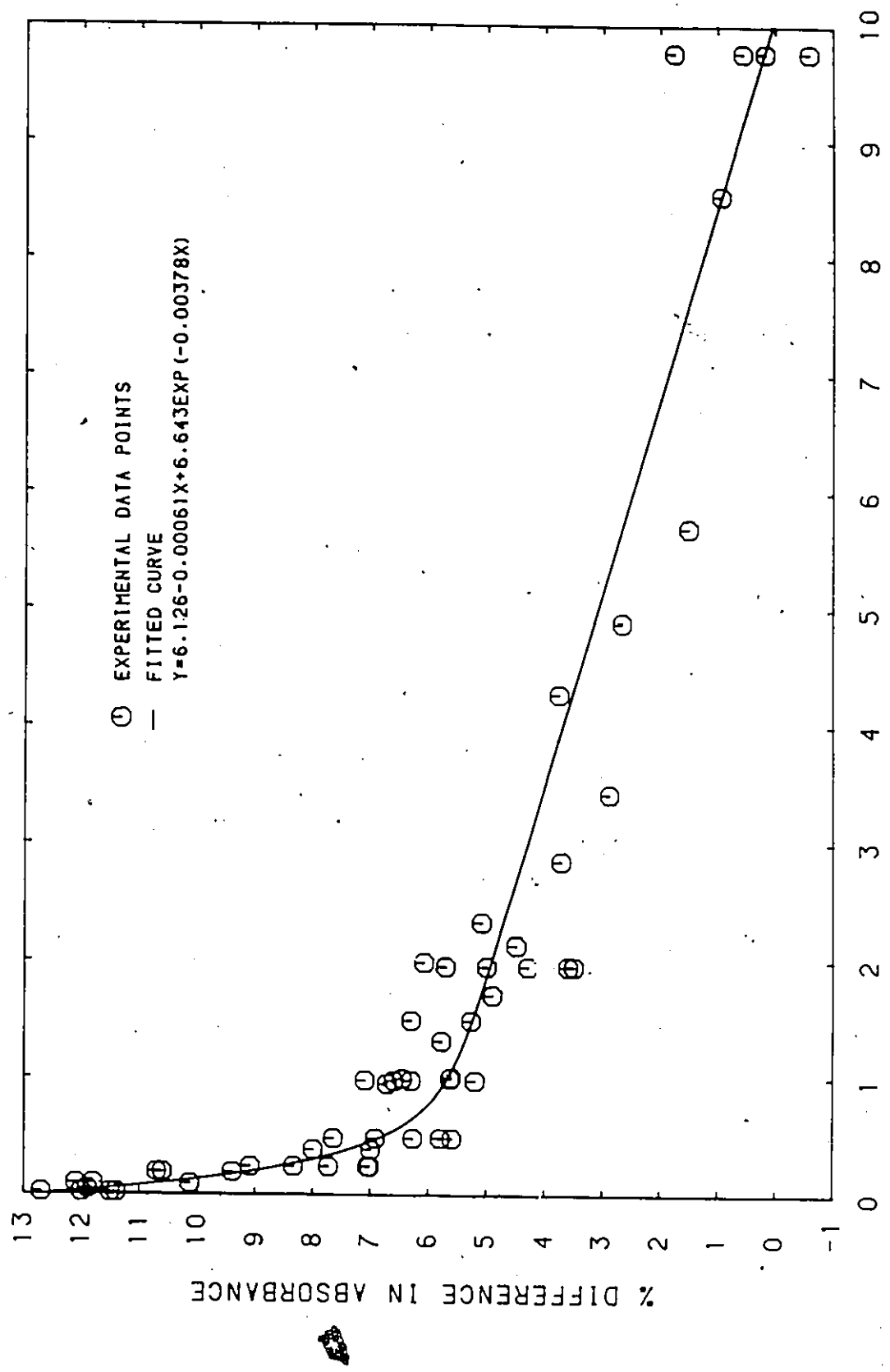


FIGURE 29. SODIUM CORRECTION FACTOR FOR THE ABSORBANCE OF NICKEL

Various empirical models were used to try to adequately represent this data. The selection criteria involved examining residual plots, precision of the parameter estimates, correlations between parameter estimates and the results of an R-test. The R-test is a quantitative lack of fit test in which the ratio of the sum of squares due to lack of fit to the sum of squares due to pure error is compared to the upper α % value of the F-statistic. If the ratio is greater than the F-stat the model displays a significant lack of fit. The R-test is only approximate for nonlinear models and makes use of the assumptions in the results and discussion section. In any case both models showed no signs of inadequacy. The experimental data is shown in Tables 53 and 54 while the following tables show the chosen models and their associated parameter values.

Using the data from Table 27 the correction factors for cobalt and nickel can now be determined. It should be noted that PER is the % difference between the absorbances of standards with sodium and absorbances of standards without sodium.

$$PER_A = \phi_1 + \phi_2 DF_A + \phi_3 \exp(-\phi_4 DF_A)$$

$$PER_{Co} = 2.830 - 0.0002442(1600) + 8.687 \exp(-.001849(1600))$$

$$PER_{Co} = 2.89\ \%$$

$$PER_{Ni} = 6.126 - 0.0006073(200) + 6.643 \exp(-.003781(200))$$

$$PER_{Ni} = 9.12\ \%$$

Now the corrected absorbances (CABS's) can be determined.

Table 28: THE SODIUM CORRECTION FACTOR FOR COBALT

$PER = \phi_1 + \phi_2 DF + \phi_3 \exp(-\phi_4 DF)$

COBALT

PARAMETER ESTIMATES		L95	U95
ϕ_1	+2.830	1.9	3.7
ϕ_2	-0.0002442	-0.00042	-0.000072
ϕ_3	+8.687	7.7	9.6
ϕ_4	+0.001849	0.0013	0.0024

CORRELATIONS

$\phi_1\phi_2$	-0.725
$\phi_1\phi_3$	+0.794
$\phi_1\phi_4$	-0.865
$\phi_2\phi_3$	-0.311
$\phi_2\phi_4$	+0.656
$\phi_3\phi_4$	-0.622
SSR	45.5
n	57

$$CABS_A = ABS_A / (1 + PER_A / 100)$$

$$CABS_{Co} = 133.4 / (1 + 2.89 / 100) = 129.7$$

$$CABS_{Ni} = 128.6 / (1 + 9.12 / 100) = 117.9$$

As mentioned previously, calibration curves were made by measuring the absorbance of standards of known concentrations and then plotting absorbance vs. metal concentration in ppm.

Linear least squares (see Appendix B) was used to fit a straight line to this data which followed Beer's law from about 1 to 6ppm (for Co

Table 29: THE SODIUM CORRECTION FACTOR FOR NICKEL

$PER = \phi_1 + \phi_2 DF + \phi_3 \exp(-\phi_4 DF)$

NICKEL

PARAMETER ESTIMATES		L95	U95
ϕ_1	+6.126	5.6	6.7
ϕ_2	-0.0006073	-0.00072	-0.000049
ϕ_3	+6.643	5.7	7.6
ϕ_4	+0.003781	0.0025	0.0050

CORRELATIONS

$\phi_1\phi_2$	-0.380
$\phi_1\phi_3$	+0.611
$\phi_1\phi_4$	-0.762
$\phi_2\phi_3$	+0.256
$\phi_2\phi_4$	+0.308
$\phi_3\phi_4$	-0.427
SSR	39.4
n	53

and Ni). The calibration curve for cobalt for the data point used in this sample calculation is given below.

The 95 % confidence interval lines are shown for a future prediction of the absorbance or the response variable. These confidence intervals are for predicting the absorbance from a known cobalt concentration. Since the measured absorbance is actually used to determine the concentration an approximate confidence interval could be determined for the concentration by drawing horizontal lines from the calibration curve to the confidence interval lines at the measured absorbance (ABS) and reflect-

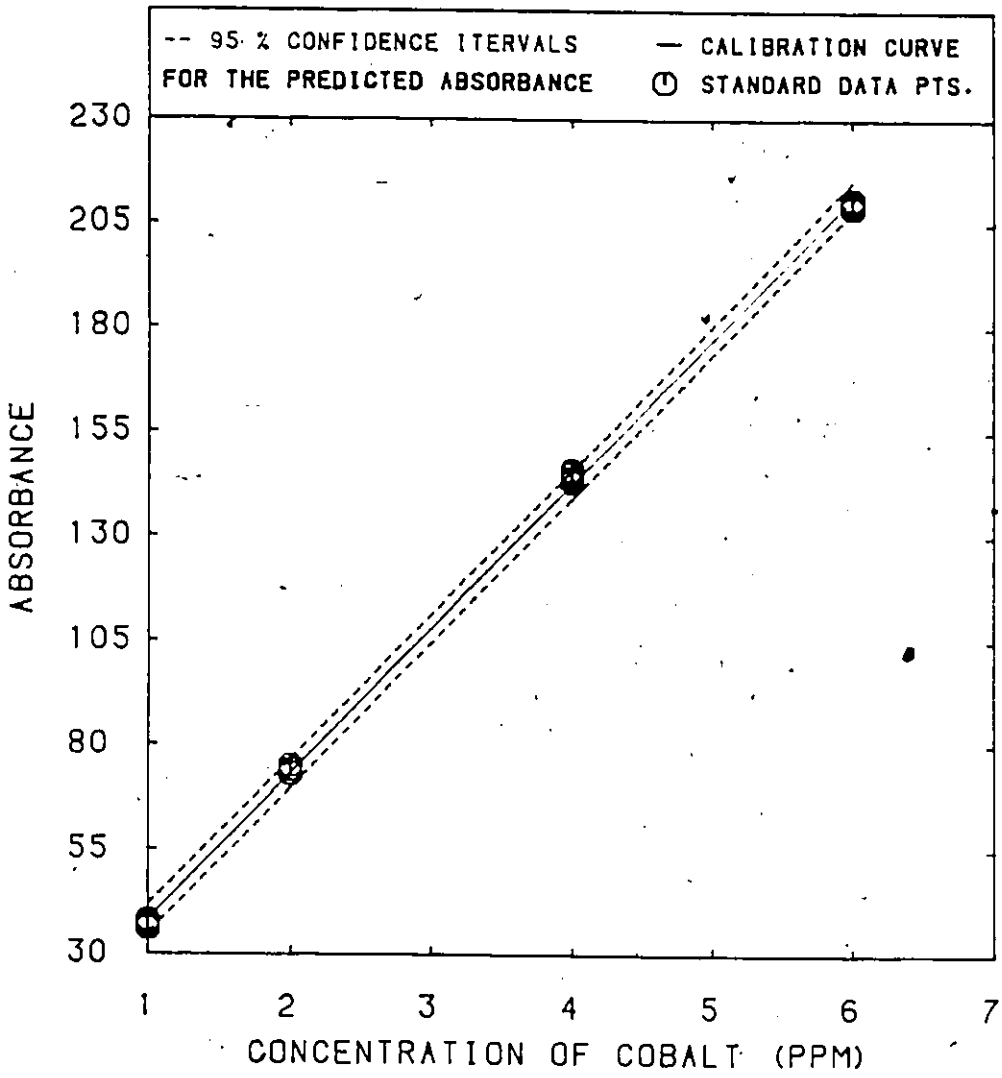


FIGURE 30. SAMPLE CALIBRATION CURVE FOR THE ATOMIC ABSORPTION SPECTROPHOTOMETER

ing these vertically to the x-axis. However, due to the fact that a method had to be devised to take into account the affect of sodium and that this method added a significant amount of uncertainty about the precision of the absorbance readings, no estimate of this precision will be given. Suffice it to say that, since the absorbance readings from the AAS usually had 3 significant figures, the corresponding equilibrium concentrations could be reported, at most, to 3 significant figures. All calculations, however, were performed with as many significant figures as allowed by the computer and the final answers were rounded off to 3 significant figures. For this reason some round off errors may be found in the following calculations.

The following calibration equations were obtained for cobalt and nickel.

$$ABS_{Co} = 34.653(\text{Concentration of Co (ppm)}) + 3.7136$$
$$ABS_{Ni} = 26.833(\text{Concentration of Ni (ppm)}) + 0.5681$$

Since the product of the concentration in ppm and the dilution factor divided by 1000 is equal to the concentration in g/l the following equilibrium concentrations were obtained.

$$X'_{Co} = ((129.7 - 3.7136) / 34.653) \times 1600 / 1000 = 5.81 \text{ g/l}$$
$$X'_{Ni} = ((117.9 - 0.5681) / 26.833) \times 200 / 1000 = 0.874 \text{ g/l}$$

Now the organic phase concentrations can be determined from mass balances using the information from table 27.

$$Y'_{Co} = 16.1846 \text{ g/l} - 5.81 \text{ g/l} = 10.4 \text{ g/l}$$

$$Y'_{Ni} = 2.3267 \text{ g/l} - 0.874 \text{ g/l} = 1.45 \text{ g/l}$$

The mole fractions are as follows;

$$x_{Co} = (5.81 / 58.933) / ((5.81 / 58.933) + (0.874 / 58.71)) = 0.869$$

$$x_{Ni} = (0.874 / 58.71) / ((5.81 / 58.933) + (0.874 / 58.71)) = 0.131$$

$$y_{Co} = (10.4 / 58.933) / ((10.4 / 58.933) + (1.45 / 58.71)) = 0.877$$

$$y_{Ni} = (1.45 / 58.71) / ((10.4 / 58.933) + (1.45 / 58.71)) = 0.123$$

The pure component equilibrium concentrations are ;

$$Y' = \theta_1\theta_2X' / (1+\theta_2X') + \theta_3X'^{\theta_4}$$

$$Y^*_{Co} = 4.520(5.81) / (1+(5.81)) + 6.522(5.81)^{0.1284} = 12.0 \text{ g/l}$$

$$Y^*_{Co} = 0.204 \text{ gmol/l}$$

$$Y^*_{Ni} = 3.025(0.874) / (1+(0.874)) + 6.991(0.874)^{0.1468} = 8.26 \text{ g/l}$$

$$Y^*_{Ni} = 0.141 \text{ gmol/l}$$

Determination of the DELTA Y Functions ;

$$\Delta Y_A = Y_A - Y_A^* x_A$$

$$\Delta Y_{Co} = (10.4 / 58.933) - (0.204)(0.869) = -0.0014 \text{ gmol/l}$$

(NB. this is the value which was determined with all the decimal points allowed by the computer. Due to the rounding error involved in the subtraction process the value calculated with the above numbers which were rounded off is considerably different (-0.0008)).

$$\Delta Y_{Ni} = (1.45 / 58.71) - (0.141)(0.131) = 0.00628 \text{ gmol/l}$$

Determination of predicted DELTA Y functions ;

$$\Delta Y_A = \beta_1(1-x_A)^{\beta_2} x_A^{\beta_3} X'^{\beta_4}_B + \beta_5(1-x_A)x_A X'^{\beta_6}_B$$

$$\Delta Y_{Co} = -1.244(1-(0.869))^{1.237}(0.869)^{1.088} + (1-(0.869))(0.869)(0.874)^{0.05391} = 0.0267 \text{ gmol/l}$$

$$\Delta Y_{Ni} = -0.03500(1-(0.131))^{0.7878}(0.131) = -0.00410 \text{ gmol/l}$$

Determination of the predicted organic phase concentrations with the DELTA Y method;

$$Y_A = \Delta Y_A + Y_A^* x_A$$

$Y_{Co} = 0.0267 + (0.204)(0.869) = 0.204$ gmol/l or 12.0 g/l

$Y_{Ni} = -0.00410 + (0.141)(0.131) = 0.0144$ gmol/l or 0.843 g/l

Concentrations as predicted by the MOLE FRACTION method (with known total organic phase metal concentration Y_T = 11.85 g/l or 0.201 gmol/l) are given below.

$$y_{Co} = (x_{Co} + \lambda_1(x_{Co}^2 - x_{Co})) / (x_{Co} + (1-x_{Co}^{\lambda_2})$$

$$y_{Co} = ((0.869) - 0.3145((0.869)^2 - (0.869))) / ((0.869) + (1 - (0.869))^{1.103}) = 0.928$$

$$y_{Ni} = 1 - .928 = 0.072$$

$$Y'_{Co} = (0.928)(.201)(58.933) = 11.0 \text{ g/l}$$

$$Y'_{Ni} = (0.072)(.201)(58.71) = 0.850 \text{ g/l}$$

Actual values of the PSEUDO GAMMA functions ;

$$\gamma s_A = y_A Y_T / x_A Y_A^*$$

$$\gamma s_{Co} = (0.877)(0.201) / (0.869)(0.204) = 0.999$$

$$\gamma s_{Ni} = (0.123)(0.201) / (0.131)(0.141) = 1.34$$

PSEUDO GAMMA function predictions;

$$\gamma s_A = 1 + \alpha_1 x_B + \alpha_2 x_B^2 + \alpha_3 x_B^3 + \alpha_4 x_B^4 + \alpha_5 x_B^5$$

$$\gamma s_{Co} = 1 + 4.796(0.131) - 38.04(0.131)^2 + 123.3(0.131)^3 - 166.0(0.131)^4 + 78,91(0.131)^5 = 1.21$$

$$\gamma s_{Ni} = 1 - 7.334(0.869)^2 + 38.92(0.869)^3 - 67.72(0.869)^4 + 37.37(0.869)^5 = 0.901$$

Predictions of organic phase concentrations using the PSEUDO GAMMA Function ;

$$Y_A = \gamma_A Y_T = \gamma s_A x_A Y_A^*$$

$$Y_{Co} = (1.21)(0.869)(0.204) = 0.213 \text{ gmol/l} = 12.6 \text{ g/l}$$

$$Y_{Ni} = (0.901)(0.131)(0.141) = 0.0167 \text{ gmol/l} = 0.976 \text{ g/l}$$

Appendix E

EXPERIMENTAL DATA

The following abbreviations have been used in this Appendix;

ACT.	= ACTUAL
PRED.	= PREDICTED
RESI.	= RESIDUAL
MF	= MOLE FRACTION
GS	= PSEUDO GAMMA
DE	= DELTA Y
E	= % ERROR IN A PREDICTION

Table 30: PURE COMPONENT EQUILIBRIUM DATA FOR COBALT AT 25 DEGREES C.

X'_{Co} (g/l)	ACT. Y'_{Co} (g/l)	PRED. Y'_{Co} (g/l)	RESI. Y'_{Co} (g/l)	pH
0.0784	4.82	5.03	-0.214	6.26
0.0892	4.85	5.15	-0.300	6.48
0.142	4.75	5.63	-0.880	6.39
0.231	7.09	6.25	0.838	6.23
0.304	7.18	6.65	0.534	6.37
0.521	6.93	7.55	-0.615	6.19
0.808	9.03	8.36	0.669	6.26
0.850	9.07	8.47	0.601	6.06
3.51	11.2	11.2	-0.025	6.06
3.84	10.9	11.3	-0.418	6.10
3.86	10.8	11.3	-0.506	5.96
6.85	12.8	12.3	0.534	5.86
7.13	12.4	12.4	0.038	5.94
7.13	12.6	12.4	0.205	5.88
7.87	11.9	12.5	-0.640	5.92
11.9	12.8	13.1	-0.367	5.85
12.1	12.5	13.2	-0.683	5.70
12.3	12.4	13.2	-0.791	5.73
14.9	14.6	13.5	1.16	5.78
15.0	14.5	13.5	1.06	5.73
15.8	13.7	13.5	0.141	5.62
16.3	13.3	13.6	-0.325	5.77
16.5	13.0	13.6	-0.581	5.56
19.7	14.8	13.9	0.923	5.69
19.9	14.5	13.9	0.664	5.71
20.2	14.2	13.9	0.339	5.79
20.9	13.5	14.0	-0.414	5.52
29.5	14.6	14.4	0.160	5.50
30.2	14.0	14.5	-0.515	5.63
30.3	13.9	14.5	-0.626	5.63

Table 31: PURE COMPONENT EQUILIBRIUM DATA FOR NICKEL AT 25 DEGREES C.

X'_{Ni} (g/l)	ACT. Y'_{Ni} (g/l)	PRED. Y'_{Ni} (g/l)	RESI. Y'_{Ni} (g/l)	pH
0.1068	4.90	5.32	-0.412	6.42
0.109	4.96	5.34	-0.382	6.29
0.324	7.18	6.66	0.515	6.30
0.344	7.08	6.75	0.333	6.19
1.06	8.92	8.61	0.311	6.16
1.19	8.93	8.82	0.104	5.77
1.25	8.74	8.90	-0.166	6.06
3.89	11.1	10.9	0.152	5.91
4.41	10.8	11.2	-0.376	5.93
8.03	11.9	12.2	-0.236	5.83
8.27	11.7	12.2	-0.489	5.82
11.8	13.1	12.8	0.291	5.75
12.2	12.8	12.9	-0.073	5.74
12.8	12.3	13.0	-0.636	5.71
16.0	14.0	13.3	0.648	5.69
16.2	13.7	13.4	0.351	5.69
17.3	12.7	13.5	-0.756	5.71
20.3	14.7	13.8	0.909	5.61
20.3	14.6	13.8	0.848	5.62
21.9	13.7	13.9	-0.157	5.62
25.9	14.4	14.2	0.240	5.61
26.1	14.2	14.2	0.043	5.61
31.0	14.0	14.5	-0.494	5.60
31.1	13.9	14.5	-0.603	5.59

Table 32: PURE COMPONENT EQUILIBRIUM DATA FOR COBALT AT 60 DEGREES C.

X'_{Co} (g/l)	ACT. Y'_{Co} (g/l)	PRED. Y'_{Co} (g/l)	RESI. Y'_{Co} (g/l)	pH
0.0206	4.05	5.40	-1.35	6.90
0.0225	4.05	5.71	-1.66	6.76
0.0376	7.40	7.58	-0.187	6.90
0.0413	7.39	7.93	-0.538	7.08
0.0519	10.1	8.76	1.35	6.92
0.0542	10.1	8.92	1.19	6.94
0.0670	10.1	9.65	0.444	6.95
0.206	13.4	12.6	0.729	6.48
0.211	13.5	12.7	0.799	6.49
1.65	14.4	14.6	-0.259	6.12
1.69	14.3	14.7	-0.302	6.21
4.61	14.8	15.1	-0.321	5.93
4.80	14.6	15.1	-0.533	6.07
8.06	15.4	15.4	0.006	6.01
8.22	15.3	15.4	-0.174	5.75
13.8	16.0	15.9	0.056	5.92
13.9	15.9	15.9	-0.001	5.88
17.9	16.0	16.2	-0.286	5.90
17.9	15.9	16.2	-0.338	5.95
23.9	16.3	16.7	-0.411	5.85
23.9	16.3	16.7	-0.473	5.80
26.0	17.7	16.9	0.759	5.69
26.2	17.5	16.9	0.543	5.62
29.3	17.3	17.2	0.121	5.47

Table 33: PURE COMPONENT EQUILIBRIUM DATA FOR NICKEL AT 60 DEGREES C.

X'_{Ni} (g/l)	ACT. Y'_{Ni} (g/l)	PRED. Y'_{Ni} (g/l)	RESI. Y'_{Ni} (g/l)	pH
0.106	5.54	5.35	0.191	6.75
0.107	5.54	5.36	0.181	6.68
0.299	7.39	7.64	-0.248	6.75
0.299	7.39	7.64	-0.250	6.69
1.16	9.59	9.66	-0.064	6.61
1.20	9.55	9.70	-0.145	6.58
4.73	11.92	11.5	0.453	6.43
5.16	11.49	11.6	-0.120	6.51
7.45	12.40	12.3	0.147	6.34
7.59	12.26	12.3	-0.026	6.38
12.2	14.1	13.3	0.809	6.27
12.9	13.4	13.5	-0.013	6.26
14.2	13.7	13.7	0.002	6.24
14.3	13.6	13.7	-0.075	6.22
15.1	13.6	13.9	-0.240	6.15
15.2	13.6	13.9	-0.342	6.24
21.93	14.9	15.0	-0.112	6.06
22.2	14.6	15.1	-0.424	6.11
30.3	16.5	16.2	0.327	6.02

Table 34: BINARY COMPONENT EQUILIBRIUM DATA FOR COBALT AT 25 DEGREES C.

X'_{Co} (g/l)	Y'_{Co} (g/l)	pH	X'_{Ni} (g/l)	Y'_{Ni} (g/l)
0.213	1.16	5.92	2.86	8.99
1.01	3.81	6.26	2.86	7.28
2.90	7.02	6.22	2.90	4.74
2.95	7.04	6.22	2.84	4.59
6.39	8.94	5.95	2.98	3.45
11.6	12.7	6.12	2.95	1.59
16.8	14.0	6.13	2.93	1.00
23.6	14.6	6.10	2.90	0.694
27.7	16.5	5.53	2.87	1.01
0.191	0.642	5.81	5.83	10.5
0.874	2.29	5.79	5.75	9.11
3.11	5.47	6.15	5.77	7.17
6.14	6.83	5.90	5.98	5.77
11.9	10.5	6.11	5.91	2.93
17.1	12.3	5.64	6.03	2.77
22.6	13.8	5.54	5.98	2.18
23.7	15.1	5.99	5.89	1.67
28.3	15.6	6.02	5.88	1.05
0.230	0.379	5.66	11.4	12.0
0.921	1.37	5.63	11.5	11.2
3.05	3.37	6.05	11.6	9.64
5.75	5.62	5.83	11.6	8.18
12.2	8.14	5.69	12.0	5.42
17.6	10.4	5.55	12.0	4.63
25.0	13.2	5.97	12.6	3.44
22.8	12.1	5.51	12.0	4.02
28.4	14.1	5.98	11.7	2.31
0.201	0.216	5.54	23.3	13.8
1.03	0.917	5.51	23.3	13.2
2.73	2.20	5.64	23.2	11.8
2.94	2.15	5.89	22.8	12.3
3.29	2.20	5.89	23.4	11.7
5.51	3.32	5.87	24.0	10.9
5.51	3.71	5.82	23.7	11.2
5.89	3.98	5.83	23.6	11.3
12.2	5.88	5.38	24.8	8.12
17.9	7.81	5.46	23.6	7.77
23.2	9.79	5.35	23.7	6.71
28.7	11.2	5.43	24.1	5.45

Table 35: BINARY COMPONENT EQUILIBRIUM DATA FOR NICKEL AT 25 DEGREES C.

X'_{Ni} (g/l)	Y'_{Ni} (g/l)	pH	X'_{Co} (g/l)	Y'_{Co} (g/l)
0.865	1.94	6.36	2.85	9.41
2.84	4.59	6.22	2.95	7.04
2.90	4.74	6.22	2.90	7.02
3.23	4.86	5.89	3.11	6.69
5.77	7.17	6.18	3.11	5.47
6.41	7.63	6.15	3.10	5.48
11.6	9.64	6.05	3.05	3.37
16.8	11.3	5.69	2.91	2.74
22.8	12.3	5.89	2.94	2.15
29.1	12.6	5.88	3.00	1.86
0.162	0.370	5.94	5.80	11.5
0.874	1.45	5.98	5.81	10.4
3.18	3.29	6.24	5.94	9.05
5.98	5.77	5.90	6.14	6.83
11.6	8.18	5.83	5.75	5.62
17.2	9.87	5.98	5.92	4.24
23.6	11.3	5.83	5.89	3.98
28.9	12.2	5.69	6.19	2.98
0.235	0.229	5.78	11.9	13.2
1.13	0.763	5.81	11.9	12.5
2.95	1.59	6.12	11.6	12.7
3.26	1.82	6.19	12.2	12.1
5.40	3.07	6.11	11.6	10.7
5.91	2.93	6.11	11.9	10.5
6.33	3.33	5.74	12.0	10.1
12.0	5.42	5.69	12.2	8.14
18.1	7.38	5.64	12.3	6.90
24.8	8.12	5.38	12.2	5.88
29.7	9.96	5.37	12.1	5.33
0.278	0.138	5.57	23.0	15.3
0.870	0.549	5.51	23.4	14.6
2.90	0.694	6.10	23.6	14.6
3.37	0.969	5.46	23.4	14.0
5.89	1.67	5.99	23.7	15.1
12.0	4.02	5.51	22.8	12.1
12.6	3.44	5.97	25.0	13.2
18.7	4.8	5.91	25.2	12.3
23.7	6.71	5.35	23.2	9.79
29.5	7.96	5.79	24.1	9.76

Table 36: BINARY COMPONENT EQUILIBRIUM DATA FOR COBALT AT 60 DEGREES C.

X'_{Co} (g/l)	Y'_{Co} (g/l)	pH	X'_{Ni} (g/l)	Y'_{Ni} (g/l)
0.763	12.4	6.37	2.90	1.63
0.881	12.6	6.33	2.97	1.53
2.94	14.2	5.97	2.88	0.611
5.99	14.7	6.05	2.85	0.406
11.6	15.4	5.89	3.02	0.521
17.6	16.5	5.58	3.16	0.304
23.2	17.3	5.60	3.01	0.425
29.9	18.0	6.19	2.95	0.278
1.03	11.5	6.32	6.01	2.86
1.51	12.7	6.36	5.74	2.22
2.88	14.0	5.96	5.97	1.41
5.55	14.4	6.08	5.85	1.05
12.2	16.0	5.88	6.06	0.740
18.0	17.0	6.20	5.71	0.630
23.2	17.9	6.13	5.88	0.771
29.6	18.1	6.13	5.61	0.724
1.25	8.75	6.20	12.2	6.30
2.97	13.2	6.10	11.6	2.93
5.94	14.4	5.73	12.1	1.57
6.59	14.2	6.00	11.4	2.08
12.0	14.9	5.69	11.8	1.46
18.0	17.1	6.10	11.5	1.13
24.5	16.9	5.52	12.2	1.34
29.1	18.3	6.06	11.5	0.927
1.95	6.08	6.29	23.0	9.74
3.23	12.0	6.00	24.5	4.53
3.30	11.5	5.80	23.3	5.75
3.06	11.4	6.15	23.3	5.78
6.09	13.5	5.78	23.7	2.61
6.91	13.9	5.89	23.4	3.09
11.8	14.7	6.24	24.0	3.76
19.4	15.4	6.19	24.0	2.67
23.8	17.4	5.98	24.5	4.04
30.1	17.3	5.98	22.8	1.98

Table 37: BINARY COMPONENT EQUILIBRIUM DATA FOR NICKEL AT 60 DEGREES C.

X'_{Ni} (g/l)	Y'_{Ni} (g/l)	pH	X'_{Co} (g/l)	Y'_{Co} (g/l)
0.969	0.150	6.00	2.89	14.4
2.88	0.611	5.97	2.94	14.2
5.97	1.41	5.96	2.88	14.0
11.6	2.93	6.10	2.97	13.2
16.4	4.94	6.34	3.02	11.97
23.3	5.78	6.15	3.06	11.4
27.7	7.48	6.23	3.09	9.62
0.229	0.146	6.15	6.08	14.8
0.953	0.134	5.86	5.91	14.7
2.85	0.406	6.05	5.99	14.7
5.63	1.22	5.77	5.90	14.4
12.1	1.57	5.73	5.94	14.4
19.1	2.33	5.90	5.70	13.9
23.7	2.61	5.78	6.09	13.5
28.6	4.41	6.24	6.18	13.3
0.241	0.091	5.82	12.4	15.3
0.958	0.182	5.82	12.6	15.4
3.02	0.521	5.89	11.6	15.4
6.06	0.740	5.88	12.2	16.0
11.8	1.46	5.69	12.0	14.9
16.8	2.53	6.12	12.6	15.6
24.0	3.76	6.24	11.8	14.7
27.5	4.22	6.20	12.1	15.1
1.13	0.124	6.18	23.4	18.9
2.70	0.488	5.76	23.3	16.9
3.01	0.425	5.60	23.2	17.3
5.88	0.771	6.13	23.2	17.9
12.2	1.34	5.52	24.5	16.9
16.3	2.34	6.05	23.4	17.8
21.9	2.85	5.99	23.6	17.6
24.5	4.04	5.98	23.81	17.4
27.5	3.62	5.98	24.2	17.1

Table 38: ACTUAL, PREDICTED AND RESIDUAL BINARY COMPONENT EQUILIBRIUM DATA FOR COBALT AT 25 DEGREES C.

X'_{Co} (g/l)	ACT. Y'_{Co} (g/l)	PRED. Y'_{Co} (g/l)	RESI. Y'_{Co} (g/l)
0.213	1.16	0.731	0.428
1.01	3.81	3.02	0.790
2.90	7.02	6.65	0.372
2.95	7.04	6.71	0.325
6.39	8.94	10.2	-1.26
11.6	12.7	12.8	-0.102
16.8	14.0	14.1	-0.0448
23.6	14.6	15.1	-0.493
27.7	16.5	15.5	0.957
0.191	0.642	1.15	-0.511
0.874	2.29	2.57	-0.282
3.10	5.47	5.00	0.469
6.14	6.83	7.16	-0.334
11.9	10.5	10.1	0.386
17.1	12.3	12.3	0.0493
22.6	13.8	14.2	-0.372
23.7	15.1	14.6	0.549
8.3	15.6	16.0	-0.367
0.230	0.379	0.669	-0.290
0.921	1.37	1.61	-0.240
3.05	3.37	3.44	-0.0687
5.75	5.62	5.14	0.484
12.2	8.14	8.26	-0.126
17.6	10.4	10.4	-0.0113
22.8	12.1	12.3	-0.181
25.0	13.2	13.0	0.147
28.4	14.1	14.1	-0.0140
0.201	0.216	0.325	-0.108
1.03	0.917	1.04	-0.123
2.73	2.20	2.09	0.110
2.95	2.15	2.21	-0.0607
3.29	2.20	2.39	-0.192
5.51	3.32	3.45	-0.137
5.51	3.71	3.45	0.260
5.89	3.98	3.62	0.356
12.2	5.88	6.07	-0.194
17.9	7.81	8.00	-0.185
23.2	9.79	9.63	0.158
28.7	11.2	11.2	-0.0049

Table 39: ACTUAL, PREDICTED AND RESIDUAL BINARY COMPONENT EQUILIBRIUM DATA FOR NICKEL AT 25 DEGREES C.

X'_{Ni} (g/l)	ACT. Y'_{Ni} (g/l)	PRED. Y'_{Ni} (g/l)	RESI. Y'_{Ni} (g/l)
0.865	1.94	1.75	0.195
2.84	4.59	4.59	0.001
2.90	4.74	4.65	0.086
3.23	4.86	5.01	-0.158
5.77	7.17	7.17	0.001
6.41	7.63	7.59	0.046
11.6	9.64	9.88	-0.241
16.8	11.3	11.2	0.151
22.8	12.3	12.1	0.182
29.1	12.6	12.8	-0.143
0.162	0.370	0.218	0.152
0.874	1.45	1.12	0.338
3.18	3.29	3.47	-0.182
5.98	5.77	5.55	0.210
11.6	8.18	8.30	-0.124
17.2	9.87	9.99	-0.119
23.6	11.3	11.3	-0.038
28.9	12.2	12.1	0.140
0.235	0.229	0.144	0.0855
1.13	0.763	0.676	0.0873
2.95	1.59	1.67	-0.0757
3.26	1.82	1.83	-0.0099
5.40	3.07	2.86	0.209
5.91	2.93	3.09	-0.163
6.33	3.33	3.28	0.055
12.0	5.42	5.43	-0.013
18.1	7.38	7.18	0.195
24.8	8.12	8.69	-0.565
29.7	9.96	9.60	0.352
0.278	0.138	0.102	0.036
0.870	0.549	0.296	0.252
2.90	0.694	0.914	-0.220
3.37	0.969	1.05	-0.0825
5.89	1.67	1.77	-0.098
12.0	4.02	3.44	0.589
12.6	3.44	3.60	-0.160
18.7	4.80	5.21	-0.412
23.7	6.71	6.50	0.207
29.5	7.96	8.00	-0.033

Table 40: ACTUAL, PREDICTED AND RESIDUAL DELTA Y FUNCTIONS FOR COBALT AT 25 DEGREES CELSIUS

X'_{Ni} (g/l)	x_{Co}	ACT. ΔY_{Co} (gmol/l)	PRED. ΔY_{Co} (gmol/l)	RESI. ΔY_{Co} (gmol/l)
2.86	0.069	0.0125	0.0059	0.0066
2.86	0.260	0.0259	0.0057	0.0202
2.90	0.499	0.0272	0.0165	0.0107
2.84	0.508	0.0256	0.0169	0.0088
2.98	0.681	0.0109	0.0312	-.0204
2.95	0.797	0.0375	0.0364	0.0012
2.93	0.851	0.0413	0.0354	0.0060
2.90	0.890	0.0346	0.0323	0.0023
2.87	0.906	0.0589	0.0303	0.0286
5.83	0.032	0.0077	0.0058	0.0019
5.75	0.131	0.0198	0.0107	0.0092
5.77	0.349	0.0279	0.0170	0.0109
5.98	0.506	0.0119	0.0275	-.0157
5.91	0.667	0.0299	0.0391	-.0092
6.03	0.739	0.0380	0.0427	-.0047
5.98	0.790	0.0463	0.0431	0.0032
5.89	0.800	0.0646	0.0428	0.0218
5.88	0.827	0.0633	0.0420	0.0213
11.4	0.020	0.0043	0.0050	-.0007
11.5	0.074	0.0125	0.0116	0.0009
11.6	0.208	0.0186	0.0191	-.0005
11.6	0.330	0.0281	0.0255	0.0026
12.0	0.502	0.0259	0.0378	-.0120
12.0	0.593	0.0386	0.0443	-.0057
12.6	0.665	0.0633	0.0491	0.0142
12.0	0.655	0.0489	0.0480	0.0009
11.7	0.707	0.0667	0.0498	0.0169
23.3	0.009	0.0028	0.0031	-.0003
23.3	0.042	0.0093	0.0102	-.0009

TABLE 40 CONTINUED

X'_{Ni} (g/l)	x_{Co}	ACT. ΔY_{Co} (gmol/l)	PRED. ΔY_{Co} (gmol/l)	RESI. ΔY_{Co} (gmol/l)
23.2	0.105	0.0183	0.0179	0.0004
22.8	0.114	0.0154	0.0187	-.0033
23.4	0.123	0.0142	0.0197	-.0055
24.0	0.186	0.0185	0.0250	-.0065
23.7	0.188	0.0248	0.0250	-.0002
23.7	0.199	0.0268	0.0258	0.0010
24.8	0.329	0.0264	0.0359	-.0095
23.6	0.430	0.0323	0.0429	-.0106
23.7	0.494	0.0479	0.0479	0.0000
24.1	0.542	0.0574	0.0516	0.0058
0.865	0.767	0.0190	0.0236	-.0046
3.23	0.489	0.0224	0.0173	0.0051
6.41	0.325	0.0325	0.0173	0.0152
16.8	0.147	0.0195	0.0191	0.0004
29.1	0.093	0.0143	0.0180	-.0037
0.162	0.973	-0.0056	0.0100	-.0156
0.874	0.869	-0.0014	0.0267	-.0281
3.18	0.651	0.0203	0.0298	-.0096
17.2	0.256	0.0196	0.0261	-.0064
28.9	0.176	0.0144	0.0259	-.0115
0.235	0.981	0.0057	0.0084	-.0027
1.13	0.913	0.0089	0.0251	-.0162
3.26	0.789	0.0286	0.0372	-.0086
5.40	0.682	0.0299	0.0388	-.0089
6.33	0.653	0.0253	0.0391	-.0138
18.1	0.403	0.0269	0.0368	-.0099
29.7	0.288	0.0262	0.0353	-.0091
0.278	0.988	0.0240	0.0059	0.0181
0.870	0.964	0.0170	0.0145	0.0021
3.37	0.874	0.0281	0.0348	-.0068
18.7	0.573	0.0703	0.0497	0.0206
29.5	0.448	0.0581	0.0479	0.0102

Table 41: ACTUAL, PREDICTED AND RESIDUAL DELTA Y FUNCTIONS FOR NICKEL AT 25 DEGREES CELSIUS

X'_{Co} (g/l)	x_{Ni}	ACT. ΔY_{Ni} (gmol/l)	PRED. ΔY_{Ni} (gmol/l)	RESI. ΔY_{Ni} (gmol/l)
0.213	0.831	-0.0118	-0.0040	-0.0078
1.01	0.740	-0.0071	-0.0090	0.0019
2.90	0.501	-0.0082	-0.0101	0.0020
2.95	0.492	-0.0089	-0.0101	0.0013
6.39	0.319	0.0019	-0.0082	0.0102
11.6	0.203	-0.0089	-0.0059	-0.0030
16.8	0.149	-0.0094	-0.0046	-0.0048
23.6	0.110	-0.0077	-0.0035	-0.0042
27.7	0.094	0.0006	-0.0031	0.0036
0.191	0.968	-0.0131	-0.0022	-0.0108
0.874	0.869	-0.0167	-0.0062	-0.0105
3.11	0.651	-0.0067	-0.0099	0.0033
6.14	0.494	-0.0002	-0.0101	0.0099
11.9	0.333	-0.0163	-0.0085	-0.0078
17.1	0.261	-0.0049	-0.0072	0.0023
22.6	0.210	-0.0047	-0.0061	0.0015
23.7	0.200	-0.0112	-0.0059	-0.0053
28.3	0.173	-0.0164	-0.0052	-0.0112
0.230	0.980	-0.0085	-0.0016	-0.0069
0.921	0.926	-0.0115	-0.0042	-0.0073
3.05	0.792	-0.0085	-0.0081	-0.0004
5.75	0.670	-0.0069	-0.0098	0.0029
12.2	0.498	-0.0168	-0.0101	-0.0067
17.6	0.407	-0.0104	-0.0094	-0.0009
25.0	0.335	-0.0153	-0.0085	-0.0068
22.8	0.345	-0.0070	-0.0087	0.0017
28.4	0.293	-0.0248	-0.0078	-0.0170
0.201	0.991	-0.0014	-0.0008	-0.0006
1.03	0.958	-0.0043	-0.0027	-0.0015

TABLE 41 CONTINUED

X'_{Co} (g/l)	x_{Ni}	ACT. ΔY_{Ni} (gmol/l)	PRED. ΔY_{Ni} (gmol/l)	RESI. ΔY_{Ni} (gmol/l)
2.73	0.895	-0.0121	-0.0053	-0.0068
2.94	0.886	-0.0011	-0.0056	0.0045
3.29	0.877	-0.0095	-0.0059	-0.0036
5.51	0.814	-0.0088	-0.0076	-0.0012
5.51	0.812	-0.0023	-0.0076	0.0053
5.89	0.801	0.0006	-0.0079	0.0085
12.2	0.671	-0.0229	-0.0098	-0.0132
17.9	0.570	-0.0037	-0.0103	0.0066
23.2	0.506	-0.0066	-0.0102	0.0036
28.7	0.458	-0.0168	-0.0099	-0.0069
2.85	0.233	0.0003	-0.0066	0.0070
3.11	0.511	-0.0096	-0.0102	0.0006
3.10	0.675	-0.0056	-0.0098	0.0041
2.91	0.853	-0.0020	-0.0066	0.0046
3.00	0.907	-0.0072	-0.0049	-0.0023
5.80	0.027	0.0036	-0.0009	0.0046
5.81	0.131	0.0063	-0.0041	0.0104
5.94	0.349	-0.0070	-0.0087	0.0017
5.92	0.744	-0.0027	-0.0089	0.0062
6.19	0.824	0.0063	-0.0073	0.0136
11.9	0.019	0.0018	-0.0007	0.0025
11.9	0.087	0.0001	-0.0028	0.0029
12.2	0.211	-0.0072	-0.0061	-0.0011
11.6	0.318	-0.0100	-0.0082	-0.0017
12.0	0.347	-0.0128	-0.0087	-0.0041
12.3	0.597	-0.0122	-0.0102	-0.0020
12.1	0.712	-0.0055	-0.0093	0.0038
23.0	0.012	0.0010	-0.0004	0.0015
23.4	0.126	-0.0065	-0.0040	-0.0025
25.2	0.427	-0.0173	-0.0096	-0.0076
24.1	0.552	0.0001	-0.0103	0.0104
23.4	0.036	0.0043	-0.0012	0.0055

Table 42: ACTUAL, PREDICTED AND RESIDUAL DELTA Y FUNCTIONS FOR COBALT AT 60 DEGREES CELSIUS

x_{Ni} (g/l)	x_{Co}	ACT. ΔY_{Co} (gmol/l)	PRED. ΔY_{Co} (gmol/l)	RESI. ΔY_{Co} (gmol/l)
2.90	0.208	0.160	0.146	0.0143
2.97	0.228	0.158	0.147	0.0104
2.88	0.504	0.114	0.125	-0.0110
2.85	0.676	0.075	0.089	-0.0145
3.02	0.792	0.050	0.060	-0.0107
3.16	0.847	0.046	0.045	0.00120
3.01	0.885	0.044	0.034	0.0096
2.95	0.910	0.040	0.027	0.0134
6.01	0.145	0.160	0.146	0.0136
5.74	0.207	0.165	0.153	0.0113
5.97	0.325	0.155	0.154	0.0011
5.85	0.486	0.119	0.134	-0.0151
6.06	0.667	0.0937	0.0968	-0.003
5.71	0.759	0.0798	0.0725	0.0072
5.88	0.797	0.0777	0.0620	0.0158
5.61	0.840	0.062	0.049	0.0130
12.2	0.092	0.126	0.139	-0.0129
11.6	0.203	0.173	0.161	0.0118
12.1	0.329	0.160	0.162	-0.0015
11.4	0.366	0.147	0.158	-0.0111
11.8	0.502	0.119	0.139	-0.0191
11.5	0.609	0.122	0.116	0.0057
12.2	0.666	0.097	0.102	-0.0048
11.5	0.716	0.102	0.088	0.0131
24.5	0.116	0.175	0.154	0.0201
23.3	0.124	0.163	0.156	0.0069
23.3	0.116	0.164	0.154	0.0106
23.0	0.078	0.084	0.139	-0.0551

TABLE 42 CONTINUED

X'_{Ni} (g/l)	x_{Co}	ACT. ΔY_{Co} (gmol/l)	PRED. ΔY_{Co} (gmol/l)	RESI. ΔY_{Co} (gmol/l)
23.7	0.204	0.177	0.170	0.0067
23.4	0.228	0.177	0.171	0.0054
24.0	0.328	0.162	0.170	-0.0084
24.0	0.447	0.138	0.156	-0.0179
24.5	0.492	0.155	0.148	0.0071
22.8	0.568	0.127	0.132	-0.0045
0.969	0.748	0.0559	0.0662	-0.0103
16.4	0.155	0.164	0.159	0.0048
27.7	0.100	0.138	0.150	-0.0123
0.230	0.964	0.001	0.009	-0.0075
0.953	0.861	0.0275	0.0378	-0.0103
5.63	0.511	0.113	0.130	-0.0169
19.1	0.229	0.177	0.169	0.0086
28.6	0.177	0.179	0.169	0.0100
0.241	0.981	-0.0036	0.0047	-0.0083
0.958	0.929	0.0128	0.0195	-0.0067
16.8	0.428	0.150	0.155	-0.0044
27.5	0.305	0.174	0.173	0.0010
1.13	0.954	0.051	0.013	0.0386
2.70	0.896	0.033	0.031	0.0020
16.3	0.588	0.135	0.124	0.0116
21.9	0.517	0.153	0.142	0.0107
27.5	0.467	0.157	0.154	0.0027

Table 43: ACTUAL, PREDICTED AND RESIDUAL DELTA Y FUNCTIONS FOR NICKEL AT 60 DEGREES CELSIUS

X'_{Co} (g/l)	x_{Ni}	ACT. ΔY_{Ni} (gmol/l)	PRED. ΔY_{Ni} (gmol/l)	RESI. ΔY_{Ni} (gmol/l)
0.763	0.792	-0.118	-0.131	0.0131
0.881	0.772	-0.116	-0.130	0.0139
2.94	0.496	-0.0806	-0.0833	0.0028
5.99	0.324	-0.0524	-0.0482	-0.0042
11.6	0.208	-0.0295	-0.0284	-0.0011
17.6	0.153	-0.0232	-0.0204	-0.0028
23.2	0.115	-0.0140	-0.0155	0.0015
29.9	0.090	-0.0118	-0.0124	0.0005
1.03	0.855	-0.1240	-0.128	0.0041
1.51	0.793	-0.121	-0.131	0.0094
2.88	0.675	-0.112	-0.119	0.0063
5.55	0.514	-0.0856	-0.0871	0.0015
12.2	0.333	-0.0547	-0.0499	-0.0048
18.0	0.241	-0.0377	-0.0337	-0.0040
23.2	0.203	-0.0278	-0.0276	-0.0001
29.6	0.160	-0.0197	-0.0214	0.0017
1.25	0.908	-0.0986	-0.116	0.0170
2.97	0.797	-0.129	-0.131	0.0016
5.94	0.671	-0.125	-0.118	-0.0074
6.59	0.634	-0.107	-0.112	0.0047
12.0	0.498	-0.0874	-0.0837	-0.0037
18.0	0.391	-0.0687	-0.0614	-0.0072
24.5	0.334	-0.0531	-0.0502	-0.0029
29.1	0.284	-0.0479	-0.0409	-0.0070
3.23	0.884	-0.155	-0.123	-0.0321
3.30	0.876	-0.129	-0.125	-0.0047
3.06	0.884	-0.131	-0.123	-0.0082
1.95	0.922	-0.0726	-0.110	0.0370
6.09	0.796	-0.163	-0.131	-0.0318
6.91	0.772	-0.148	-0.130	-0.0179

TABLE 43 CONTINUED

X'_{Co} (g/l)	x_{Ni}	ACT. ΔY_{Ni} (gmol/l)	PRED. ΔY_{Ni} (gmol/l)	RESI. ΔY_{Ni} (gmol/l)
11.8	0.672	-0.111	-0.118	0.0066
19.4	0.553	-0.0991	-0.0954	-0.0037
23.8	0.508	-0.0644	-0.0858	0.0214
30.1	0.432	-0.0778	-0.0698	-0.0081
2.89	0.252	-0.0378	-0.0355	-0.0024
3.02	0.845	-0.119	-0.129	0.0102
3.09	0.900	-0.116	-0.118	0.0025
6.08	0.0364	-0.00193	-0.00579	0.0039
5.91	0.139	-0.0200	-0.0186	-0.0015
5.90	0.489	-0.0771	-0.0819	0.0048
5.70	0.771	-0.151	-0.130	-0.0216
6.18	0.823	-0.149	-0.131	-0.0184
12.4	0.0192	-0.0008	-0.0035	0.0027
12.6	0.0710	-0.0083	-0.0100	0.0017
12.6	0.572	-0.0951	-0.0993	0.0042
12.1	0.695	-0.116	-0.122	0.00597
23.4	0.0462	-0.0055	-0.0070	0.0016
23.3	0.104	-0.0106	-0.0141	0.00344
23.4	0.412	-0.0590	-0.0656	0.0066
23.6	0.483	-0.0747	-0.0804	0.0057
24.2	0.533	-0.0821	-0.0912	0.0091

Table 44: ACTUAL, PREDICTED AND RESIDUAL ORGANIC PHASE COBALT MOLE FRACTIONS FOR THE MOLE FRACTION METHOD AT 25 DEGREES CELSIUS

x_{Co}	ACT. y_{Co}	PRED. y_{Co}	RESI. y_{Co}
0.069	0.114	0.090	0.0242
0.260	0.343	0.328	0.0150
0.499	0.596	0.599	-0.0026
0.508	0.604	0.608	-0.0035
0.681	0.721	0.777	-0.0561
0.797	0.888	0.875	0.0130
0.851	0.933	0.915	0.0180
0.890	0.954	0.942	0.0125
0.906	0.942	0.952	-0.0101
0.032	0.057	0.041	0.0160
0.131	0.200	0.169	0.0305
0.349	0.432	0.433	-0.0008
0.506	0.541	0.605	-0.0638
0.667	0.781	0.764	0.0177
0.739	0.816	0.827	-0.0111
0.790	0.863	0.869	-0.0060
0.800	0.900	0.877	0.0228
0.827	0.937	0.898	0.0391
0.020	0.031	0.026	0.0047
0.074	0.109	0.096	0.0129
0.208	0.258	0.265	-0.0065
0.330	0.406	0.410	-0.0041
0.502	0.599	0.601	-0.0021
0.593	0.691	0.694	-0.0025
0.665	0.792	0.762	0.0305
0.655	0.750	0.753	-0.0033
0.707	0.859	0.800	0.0593
0.009	0.015	0.011	0.0042
0.042	0.065	0.055	0.0099
0.105	0.156	0.136	0.0208
0.114	0.148	0.148	0.0005

TABLE 44 CONTINUED

x_{Co}	ACT. y_{Co}	PRED. y_{Co}	RESI. y_{Co}
0.123	0.158	0.159	-0.0014
0.186	0.232	0.238	-0.0056
0.188	0.248	0.241	0.0069
0.199	0.260	0.253	0.0066
0.329	0.419	0.409	0.0100
0.430	0.500	0.524	-0.0239
0.494	0.593	0.593	-0.0006
0.542	0.672	0.643	0.0288
0.767	0.828	0.850	-0.0222
0.489	0.578	0.588	-0.0097
0.325	0.417	0.405	0.0119
0.147	0.194	0.189	0.0049
0.093	0.128	0.121	0.0070
0.973	0.968	0.989	-0.0210
0.869	0.877	0.928	-0.0508
0.651	0.733	0.749	-0.0162
0.256	0.300	0.323	-0.0229
0.176	0.195	0.225	-0.0294
0.981	0.983	0.993	-0.0101
0.913	0.942	0.956	-0.0140
0.789	0.868	0.868	0.0003
0.682	0.776	0.778	-0.0015
0.653	0.751	0.751	-0.0005
0.403	0.482	0.494	-0.0117
0.288	0.348	0.361	-0.0132
0.988	0.991	0.996	-0.0051
0.874	0.935	0.931	0.0042
0.573	0.718	0.674	0.0443
0.448	0.550	0.544	0.0062
0.964	0.964	0.985	-0.0215

Table 45: ACTUAL, PREDICTED AND RESIDUAL ORGANIC PHASE COBALT MOLE FRACTIONS FOR THE MOLE FRACTION METHOD AT 60 DEGREES CELSIUS

x_{Co}	ACT. y_{Co}	PRED. y_{Co}	RESI. y_{Co}
0.208	0.884	0.825	0.0589
0.228	0.891	0.830	0.0603
0.504	0.959	0.891	0.0671
0.676	0.973	0.929	0.0439
0.792	0.967	0.955	0.0126
0.847	0.982	0.967	0.0153
0.885	0.976	0.975	0.0012
0.910	0.985	0.980	0.0045
0.145	0.800	0.782	0.0183
0.207	0.851	0.825	0.0266
0.325	0.908	0.852	0.0555
0.486	0.932	0.888	0.0445
0.667	0.956	0.927	0.0286
0.759	0.964	0.947	0.0170
0.797	0.958	0.956	0.0029
0.840	0.961	0.965	-0.0036
0.092	0.581	0.553	0.0279
0.203	0.818	0.823	-0.0053
0.329	0.902	0.853	0.0485
0.366	0.872	0.861	0.0112
0.502	0.911	0.891	0.0195
0.609	0.938	0.914	0.0233
0.666	0.926	0.927	-0.0006
0.716	0.952	0.938	0.0136
0.116	0.726	0.701	0.0247
0.124	0.665	0.731	-0.0659
0.116	0.663	0.700	-0.0367
0.078	0.383	0.421	-0.0372
0.204	0.838	0.824	0.0141
0.228	0.817	0.830	-0.0127
0.328	0.796	0.853	-0.0574

TABLE 45 CONTINUED

x_{Co}	ACT. y_{Co}	PRED. y_{Co}	RESI. y_{Co}
0.447	0.852	0.879	-0.0266
0.492	0.811	0.889	-0.0780
0.568	0.897	0.905	-0.0084
0.083	0.511	0.466	0.0453
0.091	0.610	0.545	0.0650
0.076	0.404	0.402	0.0015
0.748	0.989	0.945	0.0444
0.155	0.707	0.795	-0.0876
0.100	0.562	0.610	-0.0480
0.964	0.990	0.992	-0.0019
0.861	0.991	0.970	0.0214
0.511	0.922	0.893	0.0287
0.229	0.856	0.831	0.0256
0.177	0.750	0.812	-0.0623
0.981	0.994	0.996	-0.0018
0.929	0.988	0.984	0.0039
0.428	0.860	0.875	-0.0145
0.305	0.781	0.848	-0.0673
0.954	0.993	0.990	0.0036
0.896	0.972	0.977	-0.0055
0.588	0.883	0.910	-0.0266
0.517	0.860	0.894	-0.0341
0.467	0.824	0.883	-0.0589

Table 46: ACTUAL, PREDICTED AND RESIDUAL PSEUDO GAMMA FUNCTIONS FOR COBALT AND NICKEL AT 25 DEGREES CELSIUS

RESI. γs_{Co}	PRED. γs_{Co}	ACT. γs_{Co}	x_{Ni}	x_{Co}	ACT. γs_{Ni}	PRED. γs_{Ni}	RESI. γs_{Ni}
0.303	2.42	2.72	0.931	0.069	0.930	0.976	-0.0466
0.222	1.39	1.61	0.740	0.260	0.947	0.923	0.0240
-0.0942	1.38	1.29	0.501	0.499	0.910	0.967	-0.0567
-0.108	1.38	1.27	0.492	0.508	0.899	0.963	-0.0640
-0.117	1.20	1.08	0.319	0.681	1.04	0.798	0.239
0.0366	1.18	1.22	0.203	0.797	0.753	0.737	0.0166
0.0108	1.20	1.21	0.149	0.851	0.646	0.836	-0.190
-0.0492	1.21	1.16	0.110	0.890	0.608	1.01	-0.398
0.056	1.20	1.26	0.094	0.906	1.04	1.11	-0.0696
0.290	3.10	3.39	0.968	0.032	0.942	0.994	-0.0516
0.220	1.75	1.97	0.869	0.131	0.913	0.943	-0.0302
0.0125	1.41	1.43	0.651	0.349	0.959	0.950	0.0087
-0.258	1.38	1.12	0.494	0.506	1.01	0.964	0.0446
-0.0038	1.21	1.21	0.333	0.667	0.762	0.816	-0.0537
0.0473	1.18	1.22	0.261	0.739	0.916	0.740	0.176
0.0630	1.18	1.24	0.210	0.790	0.900	0.733	0.168
0.150	1.18	1.33	0.200	0.800	0.726	0.739	-0.0132
0.113	1.19	1.31	0.173	0.827	0.527	0.776	-0.249
-0.319	3.37	3.05	0.980	0.020	0.969	0.997	-0.0289
-0.267	2.35	2.08	0.926	0.074	0.951	0.974	-0.0224
0.0420	1.43	1.48	0.792	0.208	0.959	0.921	0.0384
0.0214	1.41	1.43	0.670	0.330	0.961	0.943	0.0180
-0.145	1.38	1.24	0.498	0.502	0.853	0.966	-0.113
-0.0032	1.29	1.28	0.407	0.593	0.891	0.902	-0.0113
0.176	1.21	1.39	0.335	0.665	0.799	0.818	-0.0197
0.0885	1.22	1.31	0.345	0.655	0.915	0.830	0.0853
0.192	1.19	1.38	0.293	0.707	0.618	0.769	-0.150
0.519	3.66	4.18	0.991	0.009	0.992	0.999	-0.0075
-0.494	2.88	2.39	0.958	0.042	0.979	0.990	-0.0106
-0.0279	1.97	1.95	0.895	0.105	0.941	0.957	-0.0153
-0.162	1.89	1.72	0.886	0.114	0.993	0.952	0.0415

TABLE 46 CONTINUED

RESI. γs_{Co}	PRED. γs_{Co}	ACT. γs_{Co}	x_{Ni}	x_{Co}	ACT. γs_{Ni}	PRED. γs_{Ni}	RESI. γs_{Ni}
-0.199	1.81	1.61	0.877	0.123	0.952	0.947	0.0053
0.0138	1.49	1.50	0.814	0.186	0.952	0.924	0.0283
0.179	1.48	1.66	0.812	0.188	0.985	0.923	0.0620
0.216	1.45	1.67	0.801	0.199	1.00	0.922	0.0794
-0.0381	1.40	1.37	0.671	0.329	0.855	0.943	-0.0877
-0.0982	1.42	1.32	0.570	0.430	0.971	0.972	-0.0017
0.0133	1.39	1.40	0.506	0.494	0.943	0.968	-0.0250
0.0821	1.34	1.42	0.458	0.542	0.844	0.945	-0.101
-0.0466	1.18	1.13	0.233	0.767	0.976	0.729	0.248
-0.150	1.39	1.24	0.511	0.489	0.900	0.969	-0.0696
0.129	1.40	1.53	0.675	0.325	0.969	0.941	0.0279
0.0621	1.65	1.71	0.853	0.147	0.993	0.936	0.0574
-0.276	2.10	1.82	0.907	0.093	0.961	0.963	-0.0020
-0.127	1.10	0.98	0.027	0.973	2.38	1.80	0.585
-0.209	1.21	1.00	0.131	0.869	1.34	0.901	0.395
-0.0665	1.23	1.16	0.349	0.651	0.892	0.836	0.0566
-0.0064	1.39	1.38	0.744	0.256	0.988	0.922	0.0651
-0.112	1.52	1.41	0.824	0.176	1.02	0.926	0.0978
-0.0481	1.08	1.03	0.020	0.981	1.86	1.91	-0.0494
-0.152	1.20	1.05	0.087	0.913	0.978	1.16	-0.178
-.0115	1.18	1.17	0.211	0.789	0.815	0.732	0.0828
0.0039	1.20	1.20	0.318	0.682	0.849	0.797	0.0525
-0.0427	1.22	1.18	0.347	0.653	0.825	0.832	-0.0071
-0.120	1.43	1.31	0.597	0.403	0.914	0.967	-0.0533
0.0257	1.39	1.42	0.712	0.288	0.961	0.929	0.0319
0.0470	1.05	1.10	0.012	0.988	1.74	2.03	-0.290
0.0760	1.21	1.13	0.126	0.874	0.720	0.921	-0.201
0.195	1.31	1.50	0.427	0.573	0.827	0.922	-0.0945
0.118	1.42	1.54	0.552	0.448	0.993	0.974	0.0197
-0.0579	1.13	1.07	0.036	0.964	1.79	1.68	0.108

Table 47: ACTUAL, PREDICTED AND RESIDUAL PSEUDO GAMMA FUNCTIONS FOR COBALT AND NICKEL AT 60 DEGREES CELSIUS

RESI. γs_{Co}	PRED. γs_{Co}	ACT. γs_{Co}	x_{Ni}	x_{Co}	ACT. γs_{Ni}	PRED. γs_{Ni}	RESI. γs_{Ni}
-0.1779	4.31	4.13	0.792	0.208	0.191	0.262	-0.0709
-0.223	4.01	3.79	0.772	0.228	0.185	0.250	-0.0652
-0.0830	1.96	1.88	0.496	0.504	0.115	0.300	-0.1849
-0.0822	1.52	1.43	0.324	0.676	0.117	0.239	-0.122
-0.0211	1.28	1.25	0.208	0.792	0.232	0.202	0.0302
0.0467	1.17	1.22	0.153	0.847	0.183	0.228	-0.0453
0.0720	1.11	1.18	0.115	0.885	0.342	0.277	0.0647
0.0547	1.07	1.12	0.090	0.910	0.287	0.328	-0.0417
-0.0131	5.42	5.41	0.855	0.145	0.281	0.346	-0.0654
-0.1614	4.31	4.15	0.793	0.207	0.237	0.262	-0.0257
-0.0759	2.94	2.87	0.675	0.325	0.176	0.251	-0.0748
-0.0672	2.03	1.96	0.514	0.486	0.172	0.299	-0.127
0.0126	1.54	1.55	0.333	0.667	0.186	0.244	-0.0579
0.0572	1.34	1.40	0.241	0.759	0.221	0.204	0.0168
0.0823	1.27	1.35	0.203	0.797	0.320	0.202	0.117
0.0424	1.18	1.22	0.160	0.840	0.384	0.222	0.1620
-0.212	6.65	6.44	0.908	0.092	0.519	0.494	0.0245
-0.0368	4.38	4.35	0.797	0.203	0.277	0.266	0.0113
-0.0128	2.91	2.90	0.671	0.329	0.175	0.252	-0.0770
-0.0685	2.63	2.56	0.634	0.366	0.247	0.266	-0.0181
-0.0489	1.97	1.92	0.498	0.502	0.221	0.300	-0.0790
0.0785	1.67	1.75	0.391	0.609	0.218	0.274	-0.0564
-0.0287	1.54	1.51	0.334	0.666	0.299	0.245	0.0544
0.0240	1.43	1.46	0.284	0.716	0.247	0.219	0.0275
0.834	6.07	6.90	0.884	0.116	0.334	0.418	-0.0840
0.275	5.89	6.17	0.876	0.124	0.432	0.397	0.0358
0.500	6.08	6.58	0.884	0.116	0.430	0.419	0.0119
0.0062	4.37	4.37	0.796	0.204	0.215	0.265	-0.0495

TABLE 47 CONTINUED

RESI. γs_{Co}	PRED. γs_{Co}	ACT. γs_{Co}	x_{Ni}	x_{Co}	ACT. γs_{Ni}	PRED. γs_{Ni}	RESI. γs_{Ni}
0.0021	4.02	4.02	0.772	0.228	0.264	0.250	0.0137
-0.0261	2.92	2.89	0.672	0.328	0.366	0.252	0.115
-0.0479	2.19	2.14	0.553	0.447	0.316	0.293	0.0226
0.108	2.00	2.11	0.508	0.492	0.519	0.300	0.219
-0.0525	1.77	1.72	0.432	0.568	0.303	0.290	0.0130
-0.728	6.91	6.19	0.917	0.083	0.594	0.531	0.0627
-0.111	6.68	6.57	0.909	0.091	0.459	0.498	-0.0383
-0.0778	1.37	1.29	0.252	0.748	0.067	0.207	-0.140
-0.0780	5.23	5.15	0.845	0.155	0.414	0.328	0.0854
-0.0372	6.46	6.42	0.900	0.100	0.528	0.468	0.0597
-0.0023	1.01	1.01	0.036	0.964	0.567	0.501	0.0657
-0.0170	1.15	1.13	0.139	0.861	0.104	0.242	-0.1386
-0.0774	1.94	1.86	0.489	0.511	0.212	0.300	-0.0879
0.0228	3.99	4.01	0.771	0.229	0.208	0.249	-0.0415
0.1247	4.81	4.94	0.823	0.177	0.338	0.293	0.0442
-0.0017	1.00	1.00	0.019	0.981	0.662	0.579	0.0833
0.0237	1.04	1.07	0.071	0.929	0.276	0.379	-0.103
0.0758	2.27	2.35	0.572	0.428	0.311	0.288	0.0230
0.0637	3.13	3.19	0.695	0.305	0.386	0.245	0.141
0.1719	1.02	1.19	0.046	0.954	0.283	0.463	-0.180
0.0424	1.09	1.13	0.104	0.896	0.441	0.298	0.143
0.0952	1.72	1.82	0.412	0.588	0.402	0.283	0.120
0.124	1.92	2.04	0.483	0.517	0.395	0.299	0.0957
0.0793	2.10	2.18	0.533	0.467	0.432	0.297	0.135

Table 48: COMPARISON BETWEEN THE THREE METHODS FOR PREDICTING THE ORGANIC PHASE COBALT CONCENTRATIONS AT 25 DEGREES CELSIUS

X'_{Co} -- (G/L)	Y'_{Co} ACT. (G/L)	Y'_{Co} MF (G/L)	Y'_{Co} GS (G/L)	Y'_{Co} DE (G/L)	E MF %	E GS %	E DE %
0.213	1.16	0.913	1.02	0.769	-21.2	-11.8	-33.7
1.01	3.81	3.65	3.18	2.62	-4.37	-16.6	-31.2
2.90	7.02	7.05	7.50	6.39	0.42	6.81	-8.96
2.95	7.04	7.08	7.60	6.52	0.56	8.09	-7.33
6.39	8.94	9.64	9.97	10.2	7.77	11.57	13.4
11.6	12.7	12.5	12.3	12.6	-1.48	-2.45	-0.540
16.8	14.0	13.8	14.0	13.7	-1.94	-0.68	-2.50
23.6	14.6	14.4	15.2	14.5	-1.32	3.97	-0.94
27.7	16.5	16.6	15.7	14.8	1.06	-4.90	-10.2
0.191	0.642	0.463	0.587	0.529	-27.9	-8.50	-17.5
0.874	2.29	1.94	1.96	1.74	-15.3	-14.4	-23.8
3.11	5.47	5.48	5.41	4.83	0.17	-1.20	-11.7
6.14	6.83	7.63	8.45	7.75	11.8	23.8	13.5
11.97	10.5	10.3	10.6	11.1	-2.29	0.87	5.13
17.1	12.3	12.5	11.9	12.6	1.34	-3.68	2.21
22.6	13.8	13.9	13.1	13.7	0.68	-5.24	-1.36
23.7	15.1	14.7	13.4	13.8	-2.55	-11.5	-8.48
28.3	15.6	15.0	14.2	14.4	-4.18	-9.16	-8.02
0.230	0.379	0.320	0.413	0.42	-15.6	8.89	11.0
0.921	1.37	1.21	1.49	1.32	-11.8	8.92	-3.80
3.05	3.37	3.46	3.26	3.40	2.53	-3.17	0.879
5.75	5.62	5.68	5.57	5.47	1.00	-0.92	-2.74
12.2	8.14	8.16	9.14	8.84	0.32	12.3	8.67
17.6	10.4	10.4	10.5	10.7	0.34	0.417	3.22
25.0	13.2	12.7	11.5	12.3	-3.87	-13.0	-6.33
22.8	12.1	12.2	11.3	12.1	0.42	-6.95	-0.47
28.4	14.1	13.1	12.1	13.1	-6.92	-14.4	-7.07
0.200	0.216	0.157	0.189	0.24	-27.4	-12.9	8.34
1.03	0.917	0.777	1.07	0.973	-15.3	16.8	6.05

MF=MOLE FRACTION, GS=PSEUDO GAMMA, DE=DELTA Y AND E=ERROR

TABLE 48 CONTINUED

X'_{Co} (G/L)	Y'_{Co} ACT. (G/L)	Y'_{Co} MF (G/L)	Y'_{Co} GS (G/L)	Y'_{Co} DE (G/L)	E MF %	E GS %	E DE %
2.73	2.20	1.91	2.22	2.18	-13.3	0.817	-0.963
2.94	2.15	2.14	2.34	2.34	-0.32	8.98	9.10
3.29	2.20	2.22	2.47	2.52	0.94	12.2	14.7
5.51	3.32	3.40	3.30	3.70	2.38	-0.39	11.5
5.51	3.71	3.61	3.33	3.73	-2.79	-10.3	0.34
5.89	3.98	3.88	3.48	3.92	-2.53	-12.4	-1.49
12.2	5.88	5.74	6.08	6.44	-2.40	3.33	9.53
17.9	7.81	8.18	8.40	8.44	4.75	7.56	8.01
23.2	9.79	9.80	9.68	9.79	0.09	-1.17	-0.02
28.7	11.29	10.7	10.5	10.9	-4.30	-6.31	-3.04
2.85	9.41	9.66	9.74	9.68	2.66	3.60	2.88
3.11	6.69	6.80	7.47	6.39	1.65	11.7	-4.48
3.10	5.48	5.32	5.00	4.58	-2.86	-8.70	-16.3
2.91	2.74	2.67	2.63	2.72	-2.50	-4.06	-0.77
3.00	1.86	1.76	2.13	2.07	-5.51	14.7	11.6
5.80	11.4	11.6	12.9	12.3	2.16	13.7	8.10
5.81	10.4	11.0	12.6	12.0	5.78	21.6	15.9
5.94	9.05	9.24	9.62	9.61	2.18	6.37	6.22
5.92	4.24	4.57	4.29	4.62	7.64	1.06	8.93
6.19	2.98	3.43	3.24	3.66	15.1	8.68	22.8
11.9	13.2	13.3	13.9	13.4	1.02	5.25	1.19
11.9	12.5	12.7	14.4	13.5	1.48	15.1	7.62
12.2	12.1	12.1	12.3	12.6	-0.05	1.53	4.22
11.6	10.7	10.7	10.7	11.2	0.18	0.25	4.88
12.0	10.1	10.1	10.5	10.9	0.05	4.19	8.07
12.3	6.90	7.07	7.57	7.48	2.41	9.73	8.41
12.1	5.33	5.53	5.26	5.86	3.78	-1.28	10.0
23.0	15.3	15.4	14.6	14.3	0.51	-4.48	-6.96
23.4	14.0	13.9	14.9	14.4	2.46	6.47	2.85
25.2	12.3	11.5	10.7	11.1	-6.20	-13.3	-9.89
24.1	9.76	9.65	8.98	9.16	-1.15	-7.98	-6.15
23.4	14.6	14.9	15.4	14.5	2.23	5.15	-0.84

MF=MOLE FRACTION, GS=PSEUDO GAMMA, DE=DELTA Y AND E=ERROR

Table 49: COMPARISON BETWEEN THE THREE METHODS FOR PREDICTING THE ORGANIC PHASE NICKEL CONCENTRATIONS AT 25 DEGREES CELSIUS

X'_{Ni} -- (G/L)	Y'_{Ni} ACT. (G/L)	Y'_{Ni} MF (G/L)	Y'_{Ni} GS (G/L)	Y'_{Ni} DE (G/L)	E MF %	E GS %	E DE %
2.86	8.99	9.24	9.45	9.45	2.73	5.17	5.12
2.86	7.28	7.44	7.10	7.17	2.28	-2.38	-1.50
2.90	4.74	4.71	5.04	4.62	-0.62	6.41	-2.47
2.84	4.59	4.55	4.92	4.51	-0.85	7.25	-1.60
2.98	3.45	2.76	2.66	2.85	-20.1	-22.9	-17.3
2.95	1.59	1.78	1.56	1.77	11.7	-1.99	11.1
2.93	1.00	1.27	1.30	1.28	27.1	29.7	28.2
2.90	0.694	0.887	1.15	0.938	27.7	65.8	35.1
2.87	1.01	0.839	1.08	0.801	-17.2	6.88	-20.9
5.83	10.5	10.7	11.2	11.1	1.70	6.63	6.04
5.75	9.11	9.46	9.51	9.73	3.82	4.43	6.79
5.77	7.17	7.16	7.18	6.98	-0.13	0.17	-2.68
5.98	5.77	4.97	5.57	5.18	-13.9	-3.35	-10.09
5.91	2.93	3.17	3.17	3.39	8.19	8.23	15.7
6.03	2.77	2.60	2.26	2.63	-5.97	-18.3	-4.88
5.98	2.18	2.09	1.80	2.09	-4.28	-17.7	-4.12
5.89	1.67	2.06	1.72	1.98	22.9	2.91	18.6
5.88	1.05	1.70	1.56	1.71	62.0	48.8	62.7
11.4	12.0	12.1	12.6	12.4	0.49	3.89	3.39
11.5	11.2	11.3	11.5	11.6	1.44	3.24	3.83
11.6	9.64	9.55	9.33	9.66	-0.88	-3.19	0.25
11.6	8.18	8.12	8.09	8.01	-0.68	-1.05	-2.09
12.0	5.42	5.39	6.19	5.81	-0.48	14.2	7.27
12.0	4.63	4.59	4.72	4.68	-0.76	2.10	1.16
12.6	3.44	3.95	3.55	3.84	14.7	3.26	11.6
12.0	4.02	3.97	3.68	3.92	-1.27	-8.56	-2.46
11.7	2.31	3.28	2.89	3.30	42.2	25.3	43.2
23.3	13.8	13.9	14.0	13.8	0.43	0.53	0.24
23.3	13.2	13.3	13.3	13.2	1.06	0.85	0.67
23.2	11.8	12.1	12.0	12.2	2.47	1.40	3.37

MF=MOLE FRACTION, GS=PSEUDO GAMMA, DE=DELTA Y AND E=ERROR

TABLE 49 CONTINUED

X'_{Ni} -- (G/L)	Y'_{Ni} ACT. (G/L)	Y'_{Ni} MF (G/L)	Y'_{Ni} GS (G/L)	Y'_{Ni} DE (G/L)	E MF %	E GS %	E DE %
22.8	12.3	12.3	11.8	12.0	0.06	-4.36	-2.17
23.4	11.7	11.7	11.6	11.9	-0.18	-0.79	1.82
24.0	10.9	10.8	10.6	11.0	-0.72	-3.25	0.64
23.7	11.3	11.4	10.5	10.9	0.92	-6.53	-2.78
23.7	11.3	11.4	10.5	10.8	0.89	-8.12	-4.41
24.8	8.12	8.26	8.93	8.90	1.73	9.88	9.53
23.6	7.77	7.40	7.76	7.38	-4.76	-0.07	-4.98
23.7	6.71	6.70	6.87	6.50	-0.13	2.38	-3.14
24.1	5.45	5.93	6.08	5.85	8.80	11.7	7.46
0.865	1.94	1.69	1.40	1.54	-12.8	-27.9	-21.0
3.23	4.86	4.75	5.25	4.82	-2.26	8.18	-0.71
6.41	7.63	7.79	7.50	7.39	2.05	-1.79	-3.16
16.8	11.3	11.4	10.7	11.1	0.60	-5.44	-2.39
29.1	12.6	12.7	12.6	12.8	0.81	-0.47	1.08
0.162	0.370	0.125	0.283	0.103	-66.3	-23.5	-72.2
0.874	1.45	0.850	0.976	0.843	-41.1	-32.8	-42.0
3.18	3.29	3.09	3.09	3.19	-5.99	-5.98	-3.06
17.2	9.87	9.54	9.25	9.50	-3.27	-6.28	-3.70
28.9	12.2	11.8	11.0	11.4	-3.67	-10.2	-6.56
0.229	0.235	0.095	0.232	0.08	-58.7	1.05	-64.3
1.13	0.763	0.579	0.879	0.593	-24.2	15.2	-22.2
3.26	1.82	1.83	1.64	1.89	0.31	-9.78	3.49
5.40	3.07	3.05	2.91	3.17	-0.62	-5.18	3.30
6.33	3.33	3.33	3.40	3.57	-0.16	1.99	7.25
18.1	7.38	7.21	7.83	7.49	-2.24	6.09	1.58
29.7	9.96	9.76	9.55	9.73	-2.02	-4.03	-2.25
0.278	0.138	0.061	0.157	0.05	-56.2	13.6	-61.7
3.37	0.969	1.03	1.24	1.12	6.57	28.5	15.39
18.7	4.80	5.56	5.36	5.25	15.8	11.6	9.33
29.5	7.96	8.07	7.75	7.35	1.40	-2.69	-7.64
0.870	0.549	0.225	0.498	0.23	-59.0	-9.17	-58.9

MF=MOLE FRACTION, GS=PSEUDO GAMMA, DE=DELTA Y AND E=ERROR

Table 50: COMPARISON BETWEEN THE THREE METHODS FOR PREDICTING THE ORGANIC PHASE COBALT CONCENTRATIONS AT 60 DEGREES CELSIUS

X'_{Co} (G/L)	Y'_{Co} ACT. (G/L)	Y'_{Co} MF (G/L)	Y'_{Co} GS (G/L)	Y'_{Co} DE (G/L)	E MF %	E GS %	E DE %
0.763	12.4	11.6	12.7	11.6	-6.67	2.71	-6.80
0.881	12.6	11.7	13.1	11.9	-6.77	4.33	-4.86
2.94	14.2	13.2	14.7	14.8	-7.00	3.72	4.56
5.99	14.7	14.0	15.6	15.6	-4.51	6.18	5.83
11.6	15.4	15.2	15.9	16.0	-1.30	3.24	4.10
17.6	16.5	16.2	16.1	16.4	-1.56	-2.47	-0.43
23.2	17.3	17.3	16.3	16.8	-0.12	-5.94	-3.27
30.0	18.0	18.0	16.7	17.3	-0.46	-7.20	-4.38
1.03	11.5	11.2	11.4	10.7	-2.29	-1.21	-6.95
1.51	12.7	12.3	13.1	12.1	-3.12	2.58	-5.24
2.88	14.0	13.1	14.2	14.0	-6.11	1.94	-0.45
5.55	14.4	13.7	14.9	15.3	-4.77	3.73	6.16
12.2	16.0	15.6	16.2	16.2	-2.99	0.755	1.11
18.0	17.0	16.7	16.6	16.6	-1.76	-2.78	-2.50
23.2	17.9	17.8	16.8	16.9	-0.31	-5.91	-5.20
29.6	18.1	18.2	17.1	17.4	0.37	-5.69	-4.21
1.25	8.75	8.33	8.92	9.51	-4.81	1.89	8.67
2.97	13.2	13.3	13.2	12.5	0.64	0.19	-5.27
5.94	14.4	13.7	14.6	14.5	-5.38	0.854	0.633
6.59	14.2	14.1	14.7	15.0	-1.28	3.29	4.58
12.0	15.0	14.6	15.6	16.1	-2.14	4.15	7.53
18.0	17.1	16.6	16.5	16.7	-2.49	-3.18	-1.97
24.5	16.9	16.9	17.2	17.2	0.06	1.68	1.67
29.1	18.3	18.0	18.0	17.5	-1.43	-3.71	-4.23
3.23	12.0	11.6	10.5	10.8	-3.43	-12.6	-9.86
3.30	11.5	12.6	10.9	11.1	9.90	-4.96	-3.56
3.06	11.4	12.1	10.5	10.8	5.54	-8.17	-5.48
6.09	13.5	13.3	13.6	13.1	-1.68	0.31	-2.94
6.91	13.9	14.1	14.0	13.6	1.56	0.63	-2.31

MF=MOLE FRACTION, GS=PSEUDO GAMMA, DE=DELTA Y AND E=ERROR

TABLE 50 CONTINUED

X'_{Co} -- (G/L)	Y'_{Co} ACT. (G/L)	Y'_{Co} MF (G/L)	Y'_{Co} GS (G/L)	Y'_{Co} DE (G/L)	E MF %	E GS %	E DE %
11.8	14.7	15.8	15.1	15.2	7.22	2.47	3.39
19.4	15.5	15.9	16.0	16.5	3.12	3.40	6.83
23.8	17.4	19.1	16.5	17.0	9.62	-5.12	-2.42
30.1	17.3	17.4	17.4	17.5	0.94	0.41	1.53
0.944	7.44	6.78	8.20	9.03	-8.84	10.2	21.3
1.30	8.84	7.90	8.87	9.51	-10.7	0.31	7.54
2.89	14.4	13.8	15.2	15.0	-4.49	5.32	4.20
3.02	12.0	13.5	12.1	11.7	12.4	0.89	-2.36
3.09	9.62	10.5	9.62	10.4	8.55	-0.02	7.54
6.08	14.8	14.8	14.9	15.2	0.19	0.68	2.99
5.91	14.7	14.4	15.0	15.3	-2.16	1.92	4.13
5.90	14.4	14.0	15.1	15.4	-3.11	4.57	6.90
5.70	13.9	13.5	13.9	13.4	-2.99	-0.24	-3.62
6.18	13.3	14.4	13.0	12.7	8.30	-2.05	-4.43
12.4	15.3	15.3	15.5	15.8	0.18	1.77	3.20
12.6	15.4	15.4	15.3	15.8	-0.39	-0.65	2.55
12.6	15.6	15.9	15.4	15.9	1.68	-1.67	1.65
12.1	15.1	16.4	15.0	15.0	8.62	-0.46	-0.39
23.4	18.9	18.9	16.2	16.7	-0.36	-14.3	-12.0
23.3	16.9	17.0	16.3	16.8	0.56	-3.60	-0.69
23.4	17.8	18.3	16.9	17.1	3.01	-5.10	-3.84
23.6	17.6	18.3	16.6	17.0	4.0	-6.00	-3.57
24.2	17.1	18.3	16.4	16.9	7.14	-3.75	-0.92

MF=MOLE FRACTION, GS=PSEUDO GAMMA, DE=DELTA Y AND E=ERROR

Table 51: COMPARISON BETWEEN THE THREE METHODS FOR PREDICTING THE ORGANIC PHASE NICKEL CONCENTRATIONS AT 60 DEGREES CELSIUS

X'_{Ni} -- (G/L)	Y'_{Ni} ACT. (G/L)	Y'_{Ni} MF (G/L)	Y'_{Ni} GS (G/L)	Y'_{Ni} DE (G/L)	E MF %	E GS %	E DE %
2.90	1.63	2.45	2.24	0.859	50.6	37.6	-47.2
2.97	1.53	2.38	2.08	0.717	55.2	35.7	-53.3
2.88	0.611	1.60	1.60	0.450	162.	162.0	-26.4
2.85	0.406	1.07	0.833	0.653	163.	105.	61.0
3.02	0.521	0.720	0.455	0.586	38.2	-12.8	12.4
3.16	0.304	0.559	0.380	0.466	84.1	25.1	53.6
3.01	0.425	0.446	0.346	0.340	4.93	-18.7	-20.1
2.95	0.278	0.360	0.320	0.249	29.5	14.9	-10.5
6.01	2.86	3.12	3.51	2.62	9.18	22.8	-8.39
5.74	2.22	2.61	2.45	1.66	17.9	10.5	-25.0
5.97	1.41	2.26	2.01	1.04	60.1	42.0	-26.2
5.85	1.05	1.73	1.82	0.96	65.4	73.6	-8.44
6.06	0.740	1.22	0.966	1.02	64.7	30.6	38.4
5.71	0.630	0.929	0.580	0.864	47.6	-7.93	37.2
5.88	0.771	0.825	0.486	0.779	7.03	-36.9	1.00
5.61	0.724	0.657	0.417	0.624	-9.25	-42.4	-13.9
12.2	6.30	6.72	5.97	5.30	6.66	-5.17	15.9
11.6	2.93	2.85	2.80	2.84	-2.88	-4.54	-3.15
12.1	1.57	2.34	2.25	2.00	49.3	43.3	27.8
11.4	2.08	2.26	2.22	1.80	8.76	6.77	-13.2
11.8	1.46	1.78	1.98	1.68	21.8	35.1	-14.8
11.5	1.13	1.55	1.42	1.55	37.4	25.3	37.5
12.2	1.34	1.33	1.09	1.51	-0.77	-18.6	12.6
11.5	0.927	1.19	0.820	1.34	28.1	-11.6	44.4
24.5	4.53	4.94	5.69	6.41	9.06	25.7	41.6
23.3	5.75	4.62	5.29	6.02	-19.7	-7.99	4.82
23.3	5.78	5.15	5.64	6.26	-10.9	-2.45	8.34
23.7	2.61	2.84	3.22	4.48	8.68	23.4	71.6
23.4	3.09	2.88	2.94	4.14	-6.97	-4.86	33.9

MF=MOLE FRACTION, GS=PSEUDO GAMMA, DE=DELTA Y AND E=ERROR

TABLE 51 CONTINUED

X'_{Ni} -- (G/L)	Y'_{Ni} ACT. (G/L)	Y'_{Ni} MF (G/L)	Y'_{Ni} GS (G/L)	Y'_{Ni} DE (G/L)	E MF %	E GS %	E DE %
24.0	3.76	2.70	2.59	3.37	-28.1	-31.0	-10.3
24.0	2.67	2.19	2.49	2.88	-18.0	-6.82	8.03
24.5	4.04	3.37	2.34	2.78	-41.2	-42.0	-31.1
22.8	1.98	1.81	1.90	2.45	-8.19	-4.05	23.9
10.5	7.10	7.75	6.31	5.33	9.23	-11.0	-25.0
12.9	5.64	6.58	6.08	5.45	16.7	7.89	-3.27
0.969	0.156	0.801	0.492	0.296	412.	215.	89.0
16.4	4.94	3.46	3.91	4.34	-29.9	-20.9	-12.2
27.7	7.48	6.66	6.68	7.33	-11.0	-10.7	-1.94
0.229	0.146	0.118	0.130	-0.081	-18.9	-11.07	-156.
0.953	0.134	0.451	0.318	0.220	236.	137.	64.1
5.63	1.22	1.67	1.72	0.942	36.6	41.0	-22.8
19.1	2.33	2.75	2.80	3.60	17.8	19.9	54.4
28.6	4.41	3.31	3.86	5.48	-24.9	-12.4	24.5
0.241	0.091	0.064	0.080	-0.07	-29.4	-11.9	-172.
0.958	0.182	0.242	0.254	0.080	33.0	39.6	-55.9
16.8	2.53	2.26	2.33	2.28	-10.3	-7.58	-9.81
27.5	4.22	2.93	2.70	3.87	-30.7	-36.1	-8.30
1.13	0.124	0.192	0.206	0.033	54.9	65.8	-73.7
2.70	0.488	0.394	0.331	0.287	-19.3	-32.2	-41.3
16.3	2.34	1.81	1.64	1.95	-22.8	-29.9	-16.6
21.9	2.85	2.16	2.17	2.52	-24.4	-24.1	-11.7
27.5	3.62	2.40	2.51	3.09	-33.5	-30.7	-14.7

MF=MOLE FRACTION, GS=PSEUDO GAMMA, DE=DELTA Y AND E=ERROR

Table 52: SAMPLE DATA FOR THE ATOMIC ABSORPTION SPECTROPHOTOMETER

CONC. (ppm)	ACT. ABS.	PRED. ABS.	RESI. ABS.
1.0	37	38.4	-1.4
1.0	37	38.4	-1.4
1.0	36	38.4	-2.4
1.0	37	38.4	-1.4
1.0	37	38.4	-1.4
1.0	38	38.4	-0.4
2.0	73	73.0	-0.02
2.0	74	73.0	0.98
2.0	74	73.0	0.98
2.0	75	73.0	2.0
2.0	73	73.0	-0.02
2.0	73	73.0	-0.02
4.0	144	142.3	1.7
4.0	144	142.3	1.7
4.0	146	142.3	3.7
4.0	143	142.3	0.7
4.0	145	142.3	2.7
4.0	144	142.3	1.7
4.0	143	142.3	0.68
6.0	209	211.6	-2.6
6.0	211	211.6	-0.63
6.0	210	211.6	-1.6
6.0	211	211.6	-0.63
6.0	210	211.6	-1.6
6.0	211	211.6	-0.63
6.0	211	211.6	-0.63

CONC. (ppm)	UPPER 95 % PREDICTED ABS.	LOWER 95 % PREDICTED ABS.
1.0	42.	35.
2.0	77.	70.
4.0	146.	139.
6.0	215.	208.

Table 53: THE SODIUM CORRECTION FACTOR FOR COBALT

DILUTION FACTOR	ACTUAL % DEVIATION IN ABS.	PREDICTED % DEVIATION IN ABS.	RESIDUAL % DEVIATION IN ABS.
19.53	10.70	11.20	-0.50
19.53	10.50	11.20	-0.70
19.53	10.50	11.20	-0.70
19.53	12.00	11.20	0.80
19.53	10.30	11.20	-0.90
48.83	11.30	10.75	0.55
97.67	10.90	10.06	0.84
97.67	11.30	10.06	1.24
97.67	11.20	10.06	1.14
97.67	11.40	10.06	1.34
97.67	9.60	10.06	-0.46
195.34	7.80	8.84	-1.04
195.34	9.80	8.84	0.96
195.34	8.10	8.84	-0.74
195.34	9.50	8.84	0.66
195.34	7.60	8.84	-1.24
244.76	7.40	8.29	-0.89
244.76	6.30	8.29	-1.99
390.68	5.90	6.95	-1.05
390.68	8.50	6.95	1.55
390.68	8.50	6.95	1.55
390.68	7.80	6.95	0.85
498.31	5.18	6.17	-0.99
498.31	5.61	6.17	-0.56
948.89	4.40	4.10	0.30
976.70	4.20	4.02	0.18
976.70	3.45	4.02	-0.57
976.70	5.10	4.02	1.08

TABLE 53 CONTINUED

DILUTION FACTOR	ACTUAL % DEVIATION IN ABS.	PREDICTED % DEVIATION IN ABS.	RESIDUAL % DEVIATION IN ABS.
976.70	3.20	4.02	-0.82
994.03	4.30	3.97	0.33
994.03	3.82	3.97	-0.15
994.03	3.66	3.97	-0.31
1004.71	3.91	3.94	-0.03
1220.00	2.95	3.44	-0.49
1313.85	2.21	3.27	-1.06
1423.33	2.77	3.11	-0.34
1491.04	3.59	3.02	0.57
1491.04	4.75	3.02	1.73
1552.73	2.77	2.94	-0.17
1953.40	3.40	2.59	0.81
1953.40	4.50	2.59	1.91
1988.06	2.70	2.56	0.14
2135.00	2.61	2.48	0.13
2325.53	1.90	2.38	-0.48
2325.53	1.43	2.38	-0.95
2440.00	1.13	2.33	-1.20
2440.00	3.40	2.33	1.07
2846.60	1.06	2.18	-1.12
3422.83	1.47	2.01	-0.54
4270.00	1.73	1.79	-0.06
4883.51	2.12	1.64	0.48
4883.51	0.59	1.64	-1.05
5693.30	2.42	1.44	0.98
6569.23	1.20	1.23	-0.03
8540.00	0.20	0.74	-0.54
9767.02	0.77	0.44	0.33
9767.02	0.59	0.44	0.15

Table 54: THE SODIUM CORRECTION FACTOR FOR NICKEL

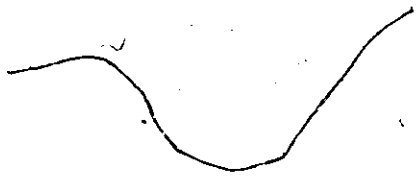
DILUTION FACTOR	ACTUAL % DEVIATION IN ABS.	PREDICTED % DEVIATION IN ABS.	RESIDUAL % DEVIATION IN ABS.
19.53	11.50	12.28	-0.78
19.53	11.40	12.28	-0.88
19.53	12.00	12.28	-0.28
19.53	12.70	12.28	0.42
48.83	11.90	11.62	0.28
97.67	11.80	10.66	1.14
97.67	10.10	10.66	-0.56
97.67	12.10	10.66	1.44
195.34	9.40	9.18	0.22
195.34	10.60	9.18	1.42
195.34	10.70	9.18	1.52
244.18	8.34	8.62	-0.28
244.18	7.73	8.62	-0.89
244.18	7.02	8.62	-1.60
244.18	9.09	8.62	0.47
244.18	7.05	8.62	-1.57
390.68	7.00	7.40	-0.40
390.68	8.00	7.40	0.60
488.35	6.92	6.88	0.04
488.35	5.60	6.88	-1.28
488.35	7.65	6.88	0.77
488.35	5.80	6.88	-1.08
488.35	6.27	6.88	-0.61
948.89	6.72	5.73	0.99
976.70	6.60	5.70	0.90
976.70	7.10	5.70	1.40

TABLE 54 CONTINUED

DILUTION FACTOR	ACTUAL % DEVIATION IN ABS.	PREDICTED % DEVIATION IN ABS.	RESIDUAL % DEVIATION IN ABS.
976.70	5.20	5.70	-0.50
976.70	6.30	5.70	0.60
994.03	5.63	5.68	-0.05
994.03	6.45	5.68	0.77
1004.71	5.61	5.66	-0.05
1313.85	5.78	5.37	0.41
1491.04	5.27	5.24	0.03
1491.04	6.30	5.24	1.06
1708.00	4.90	5.10	-0.20
1953.40	5.00	4.94	0.06
1953.40	3.60	4.94	-1.34
1953.40	3.50	4.94	-1.44
1953.40	4.30	4.94	-0.64
1953.40	5.71	4.94	0.77
1988.06	6.08	4.92	1.16
2135.00	4.50	4.83	-0.33
2325.53	5.09	4.71	0.38
2846.60	3.72	4.40	-0.68
3422.83	2.89	4.05	-1.16
4270.00	3.70	3.53	0.17
4883.51	2.67	3.16	-0.49
5693.30	1.51	2.67	-1.16
8540.00	0.95	0.94	0.011
9767.02	0.18	0.19	-0.01
9767.02	0.57	0.19	0.38
9767.02	1.76	0.19	1.57
9767.02	-0.50	0.19	-0.69

Appendix F

RESIDUAL PLOTS



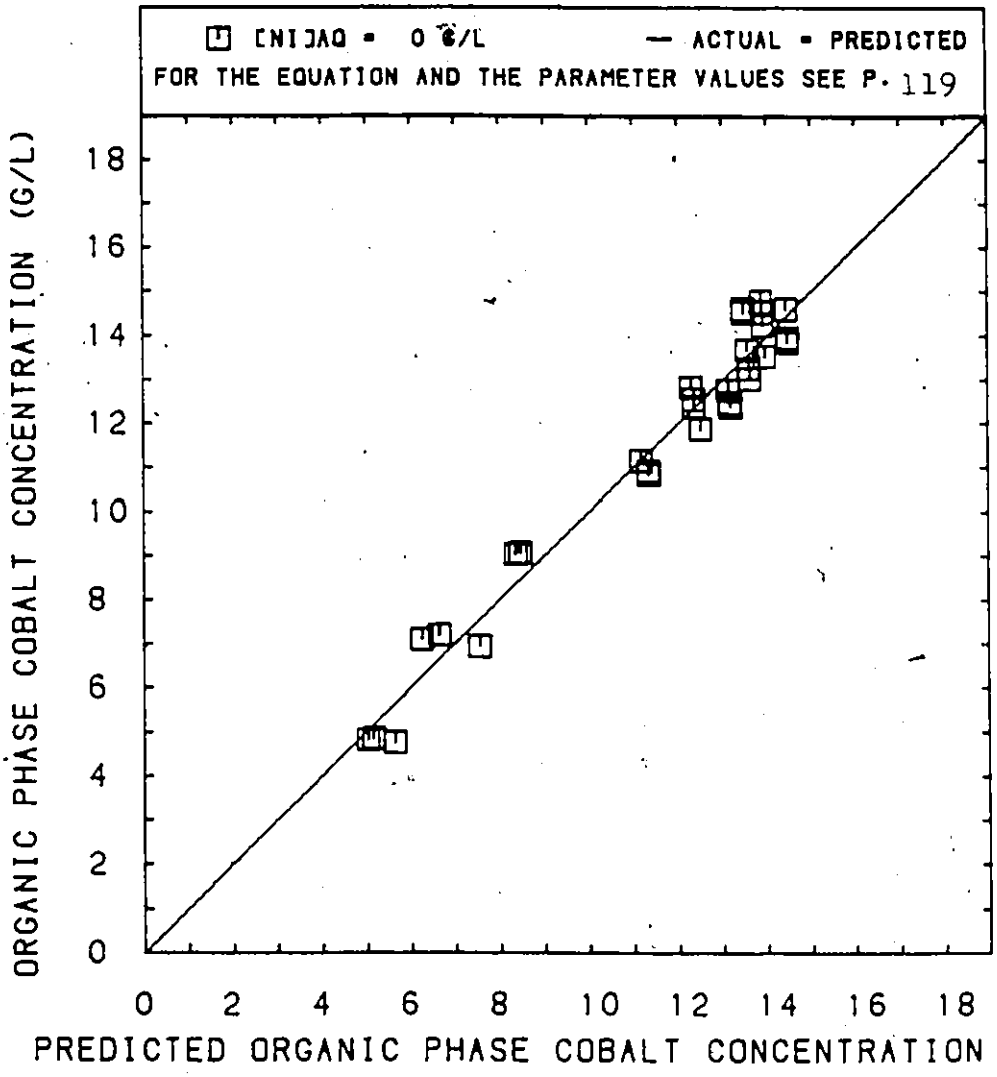


FIGURE 1A. COMPARISON BETWEEN THE ACTUAL AND PREDICTED PURE COMPONENT COBALT EXTRACTION ISOTHERMS AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.6-6.5; A/O = 1.

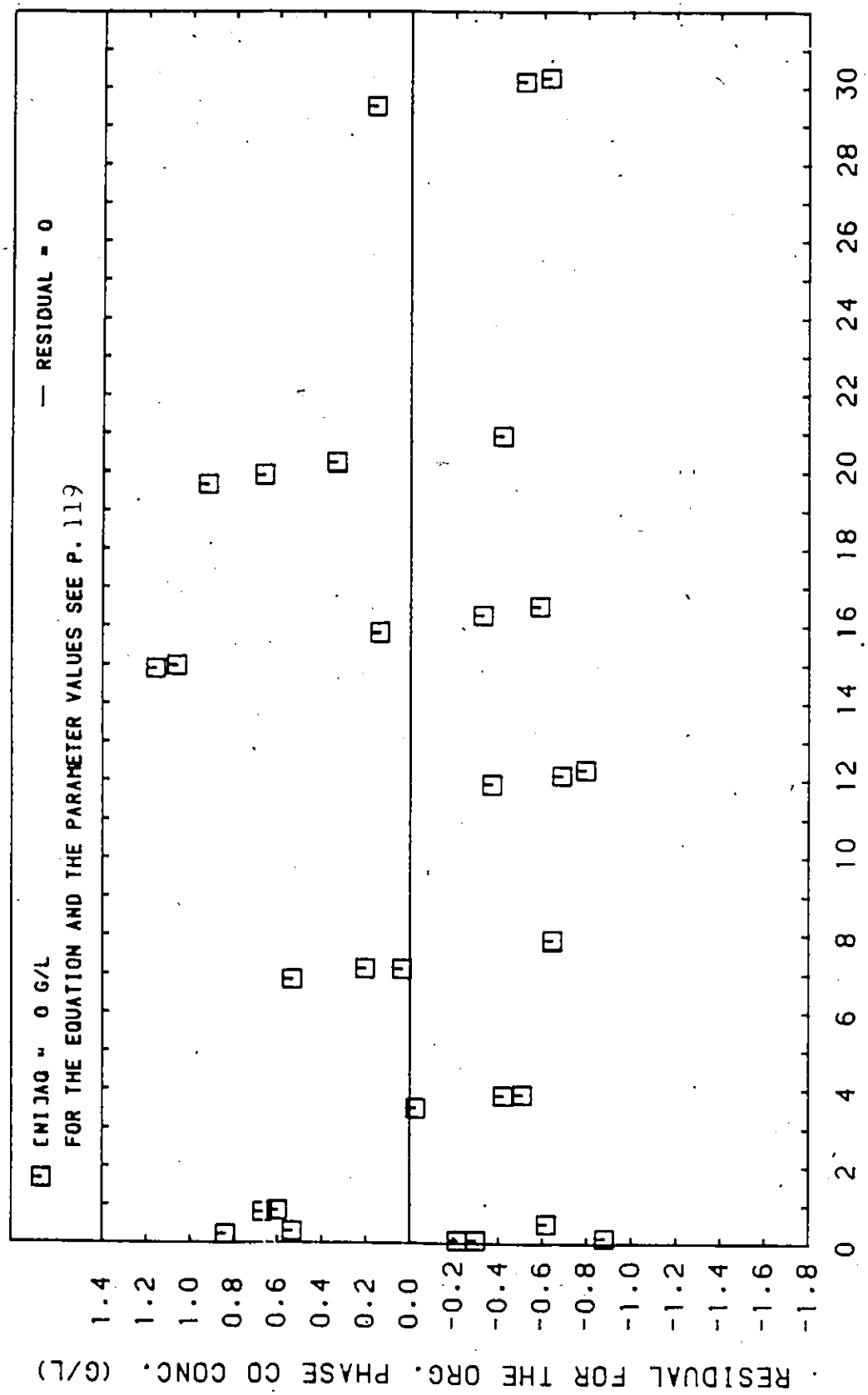


FIGURE 1B. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE PURE COMPONENT COBALT EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.6-6.5.

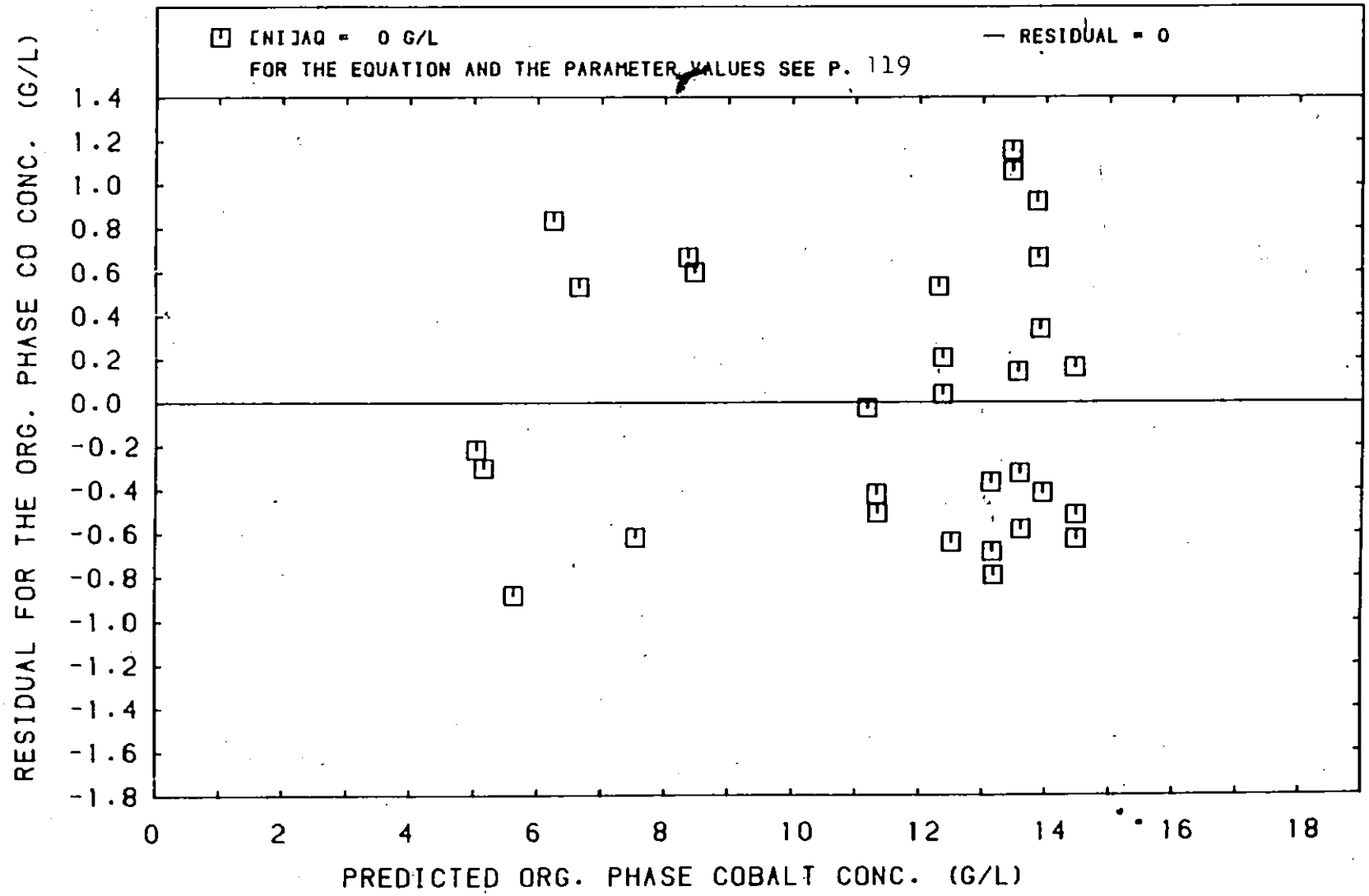


FIGURE 1C. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED PURE COMPONENT COBALT EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.6-6.5.

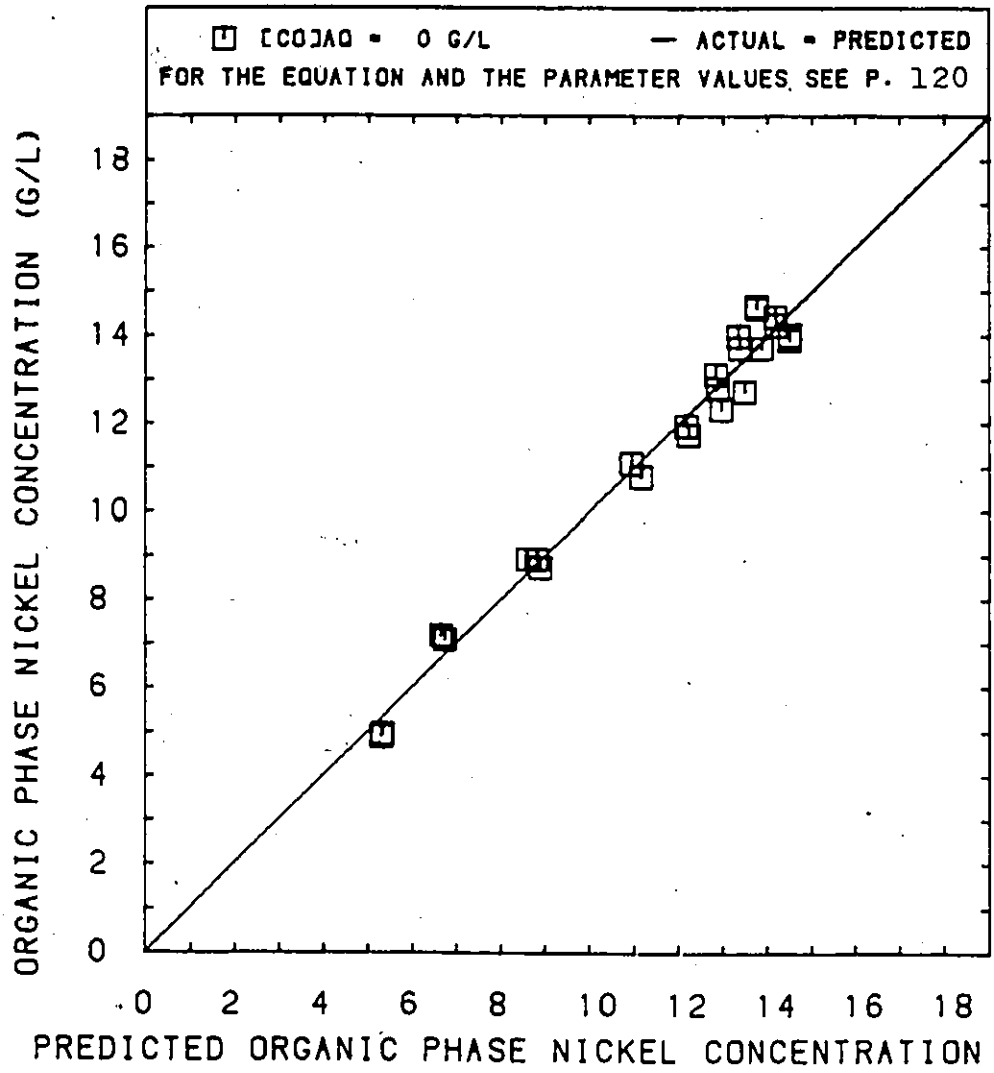


FIGURE 2A. COMPARISON BETWEEN THE ACTUAL AND PREDICTED PURE COMPONENT NICKEL EXTRACTION ISOTHERMS AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.6-6.4; A/O = 1.

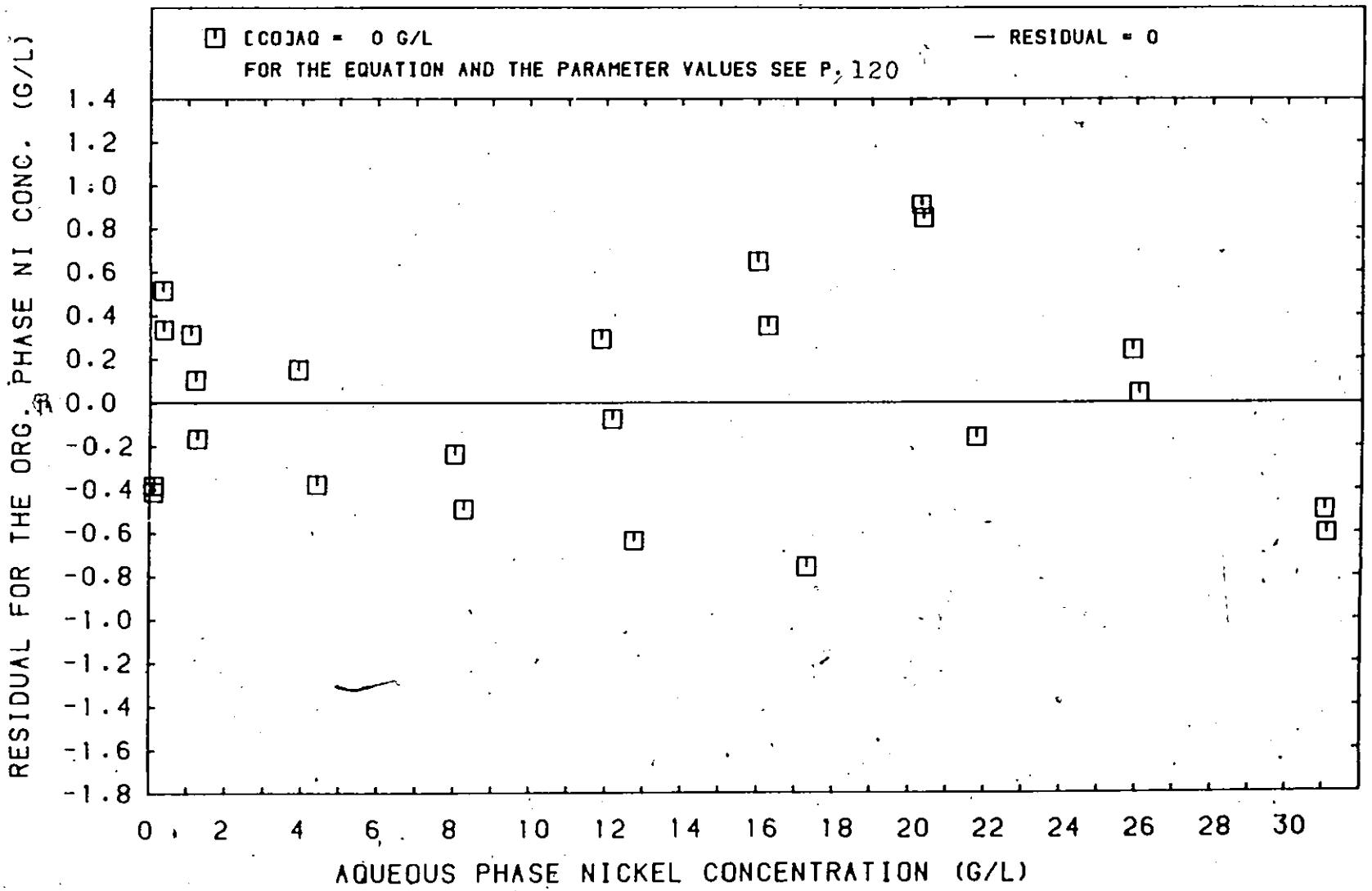


FIGURE 28. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE PURE COMPONENT NICKEL EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.6-6.4.

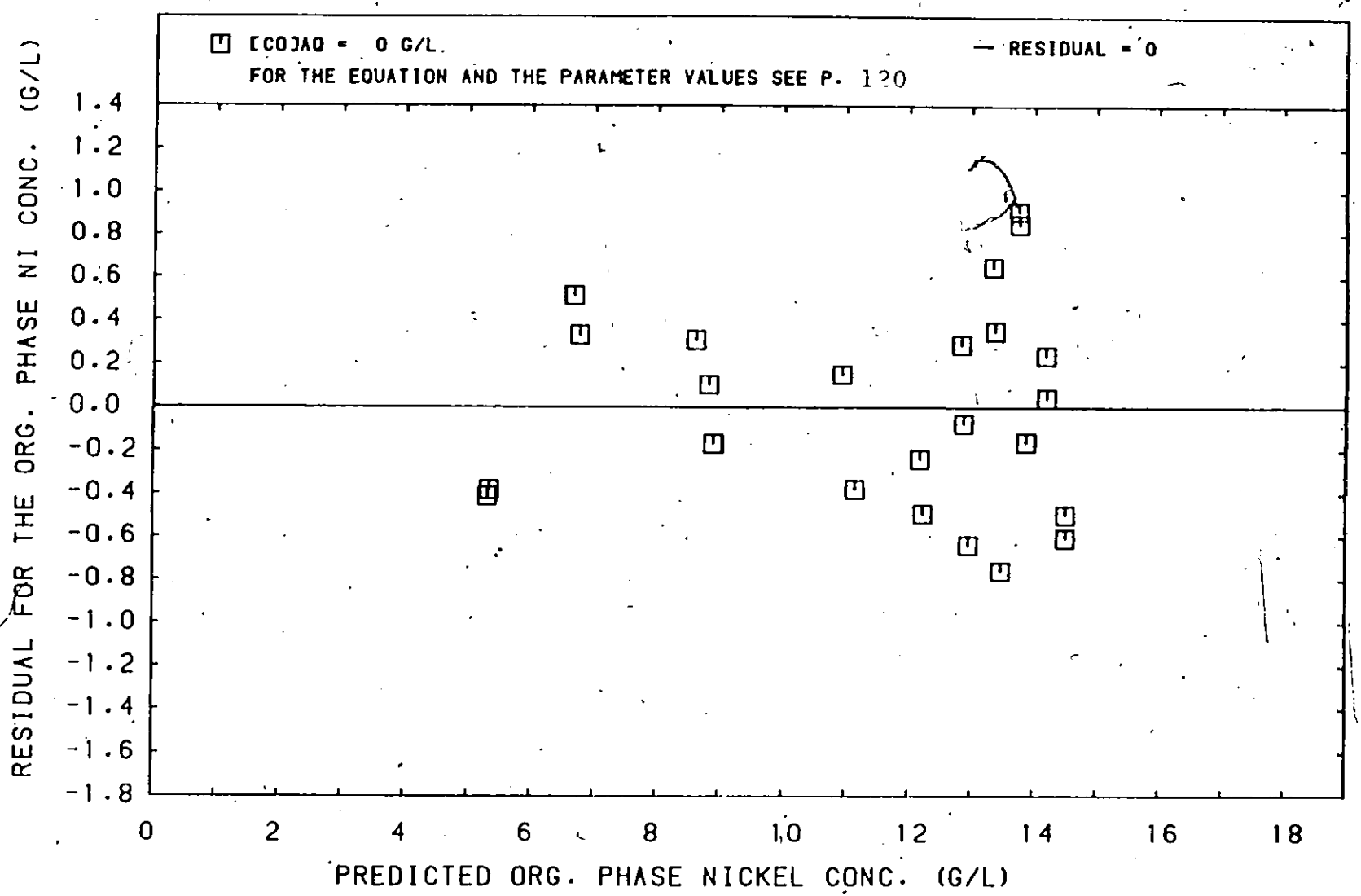


FIGURE 2C. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED PURE COMPONENT NICKEL EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.6-6.4.

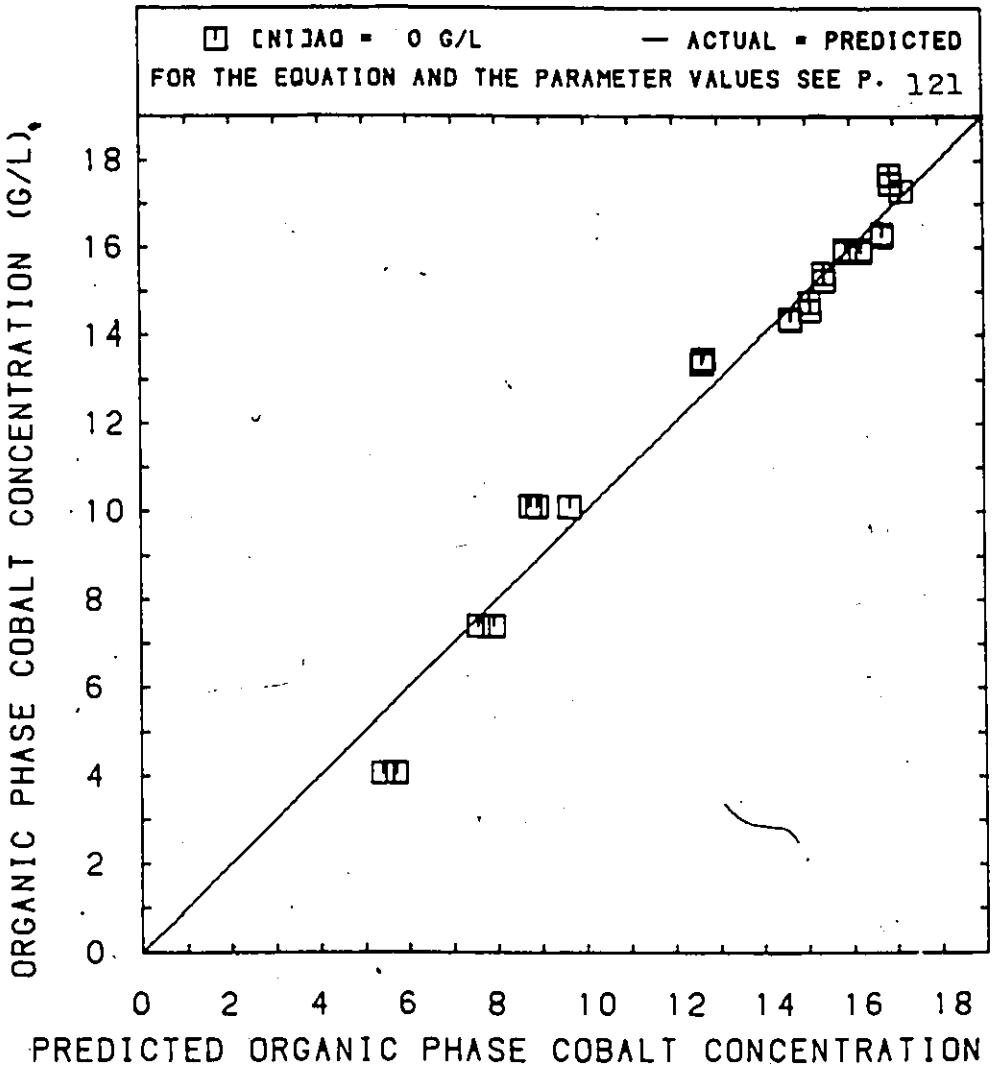


FIGURE 3A. COMPARISON BETWEEN THE ACTUAL AND PREDICTED PURE COMPONENT COBALT EXTRACTION ISOTHERMS AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.7-7.1; A/O = 1.

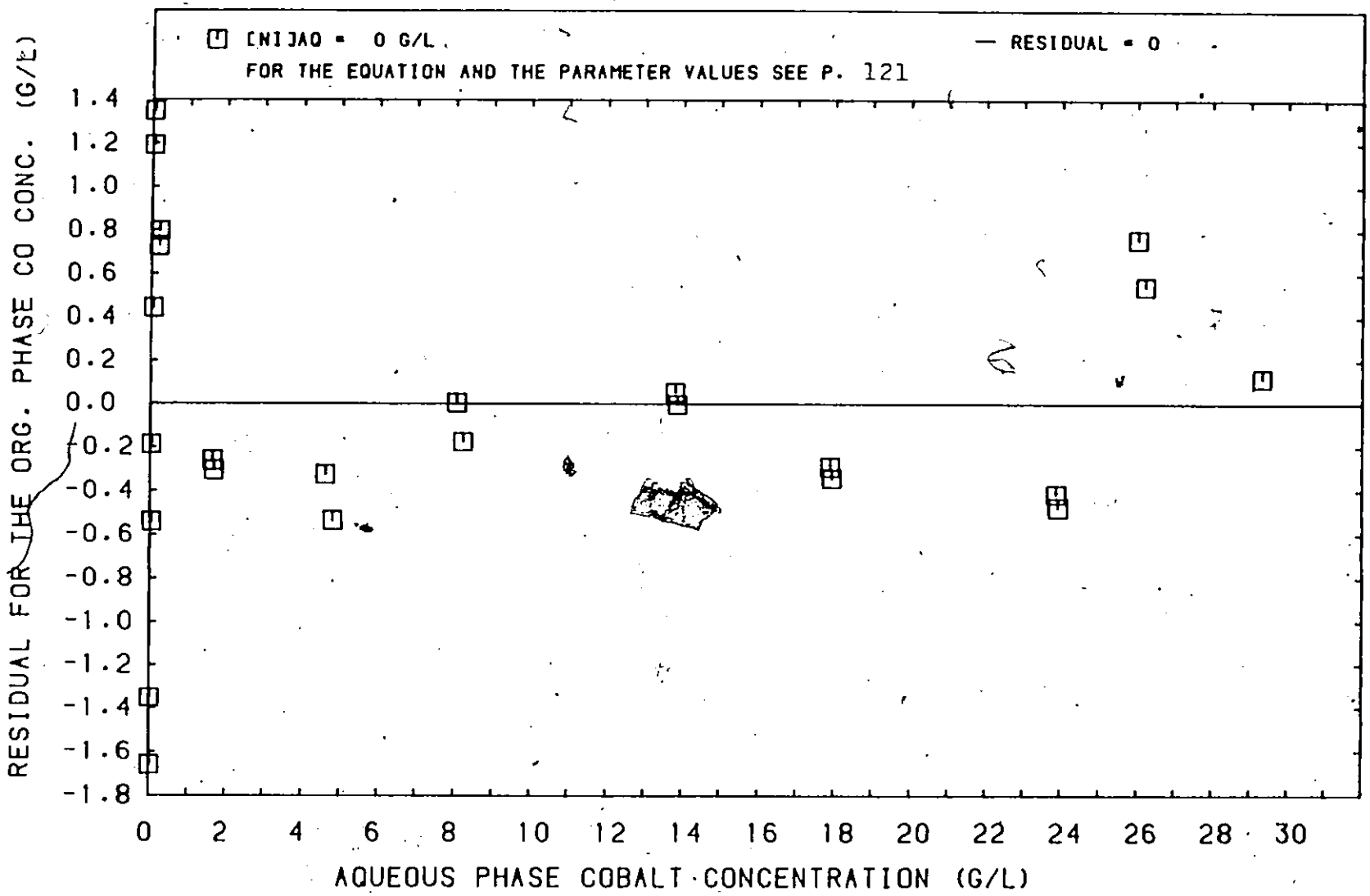


FIGURE 3B. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE PURE COMPONENT COBALT EXTRACTION ISOTHERM AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.7-7.1.

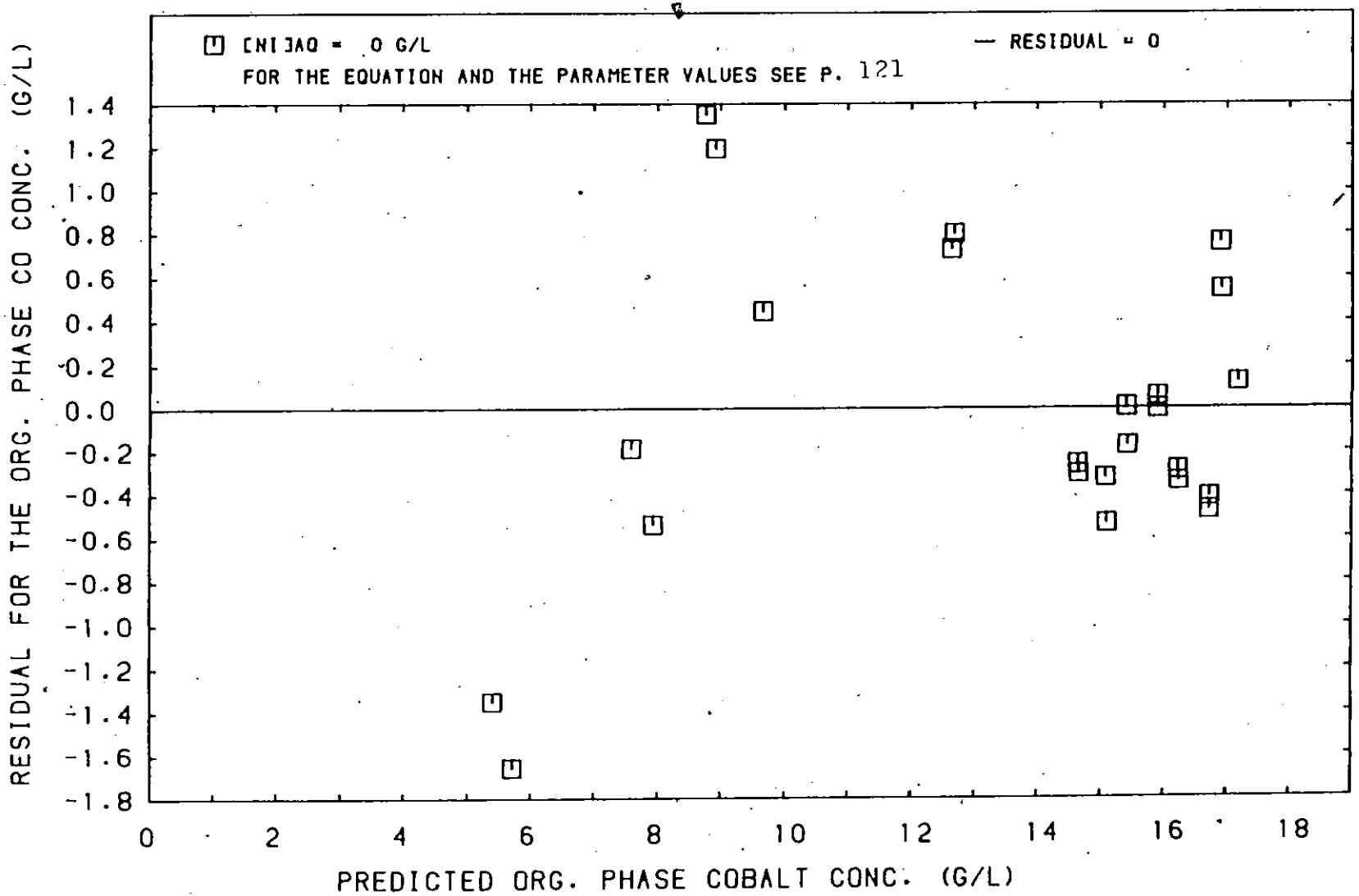


FIGURE 3C. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED PURE COMPONENT COBALT EXTRACTION ISOTHERM AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.7-7.1.

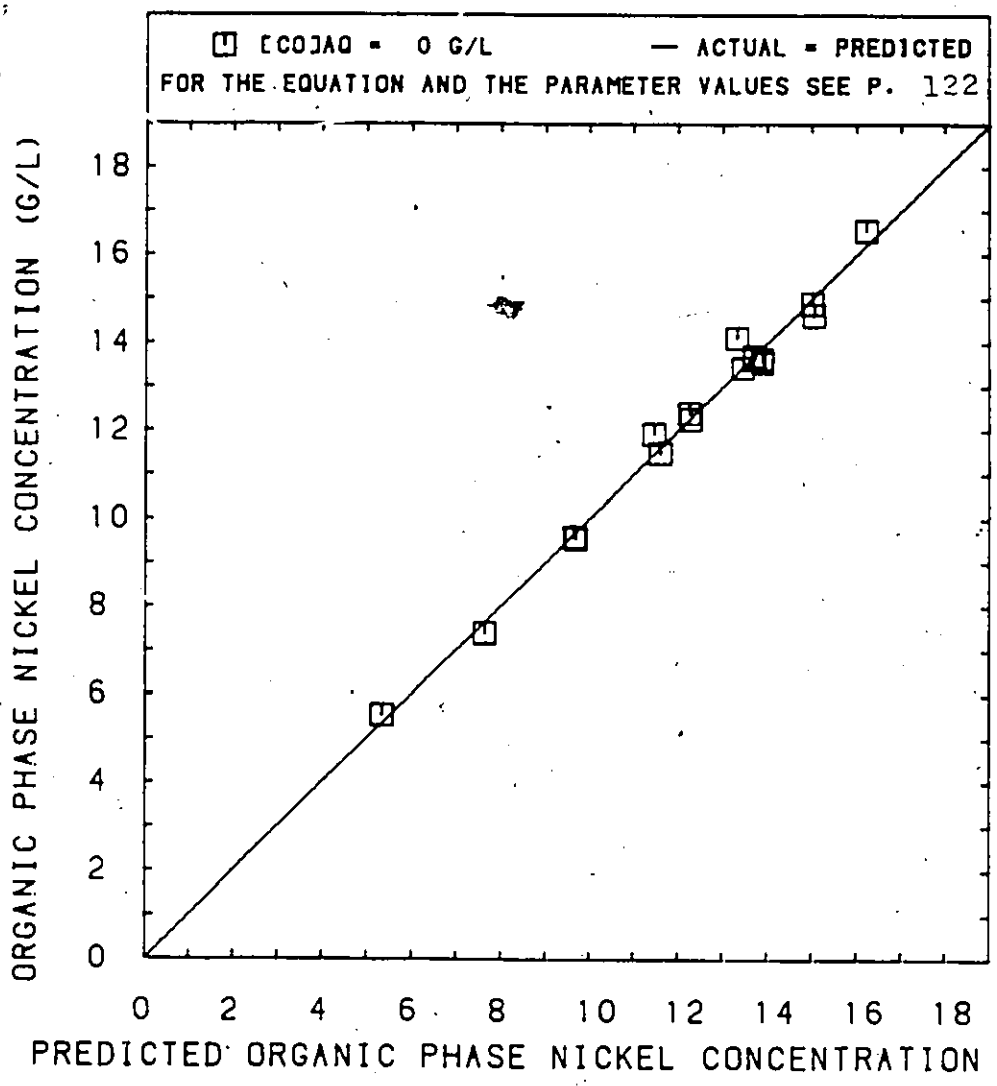


FIGURE 4A. COMPARISON BETWEEN THE ACTUAL AND PREDICTED PURE COMPONENT NICKEL EXTRACTION ISOTHERMS AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 6.0-6.8; A/O = 1.

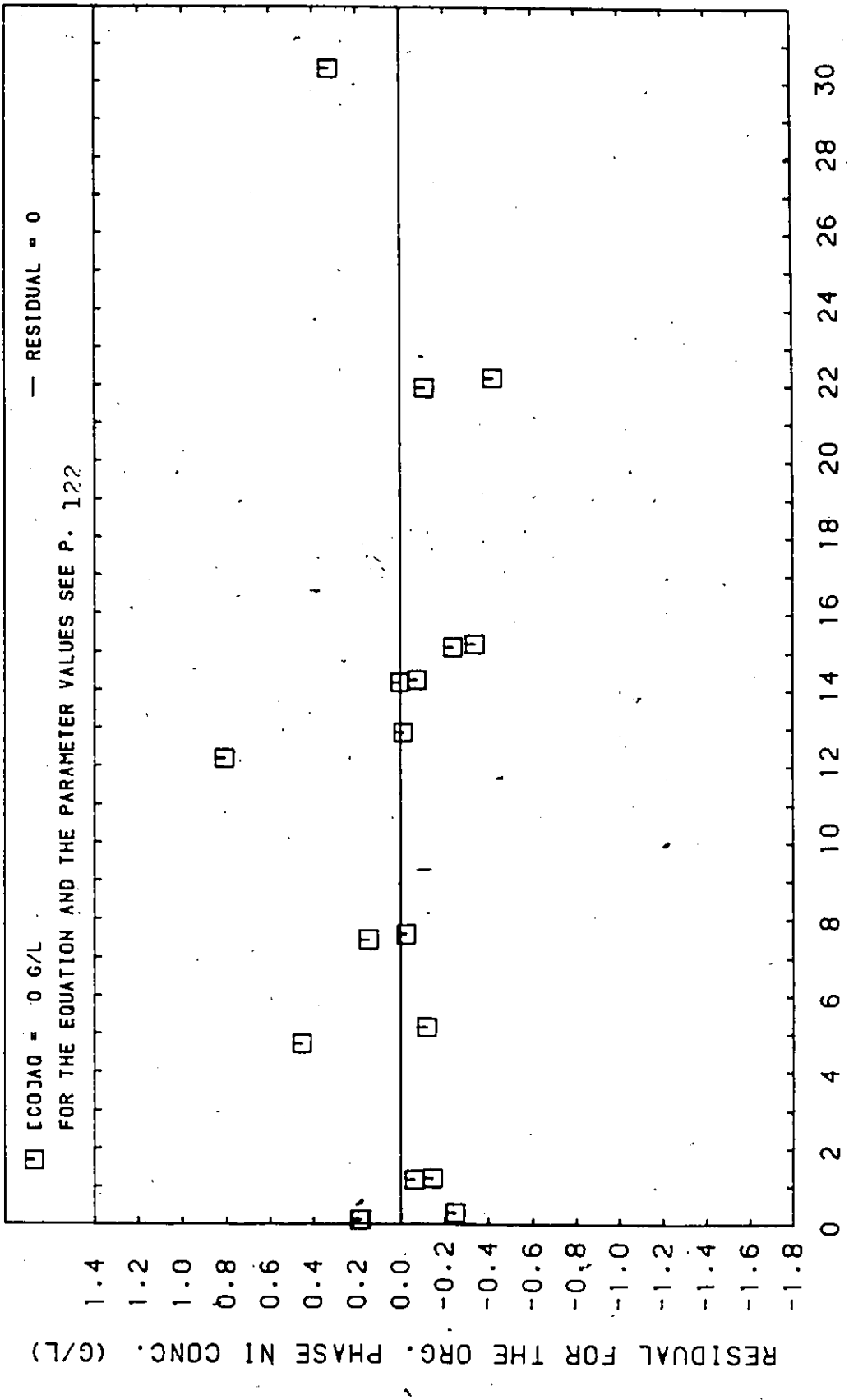


FIGURE 4B. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE PURE COMPONENT NICKEL EXTRACTION ISOTHERM AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP, A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 6.0-6.8.

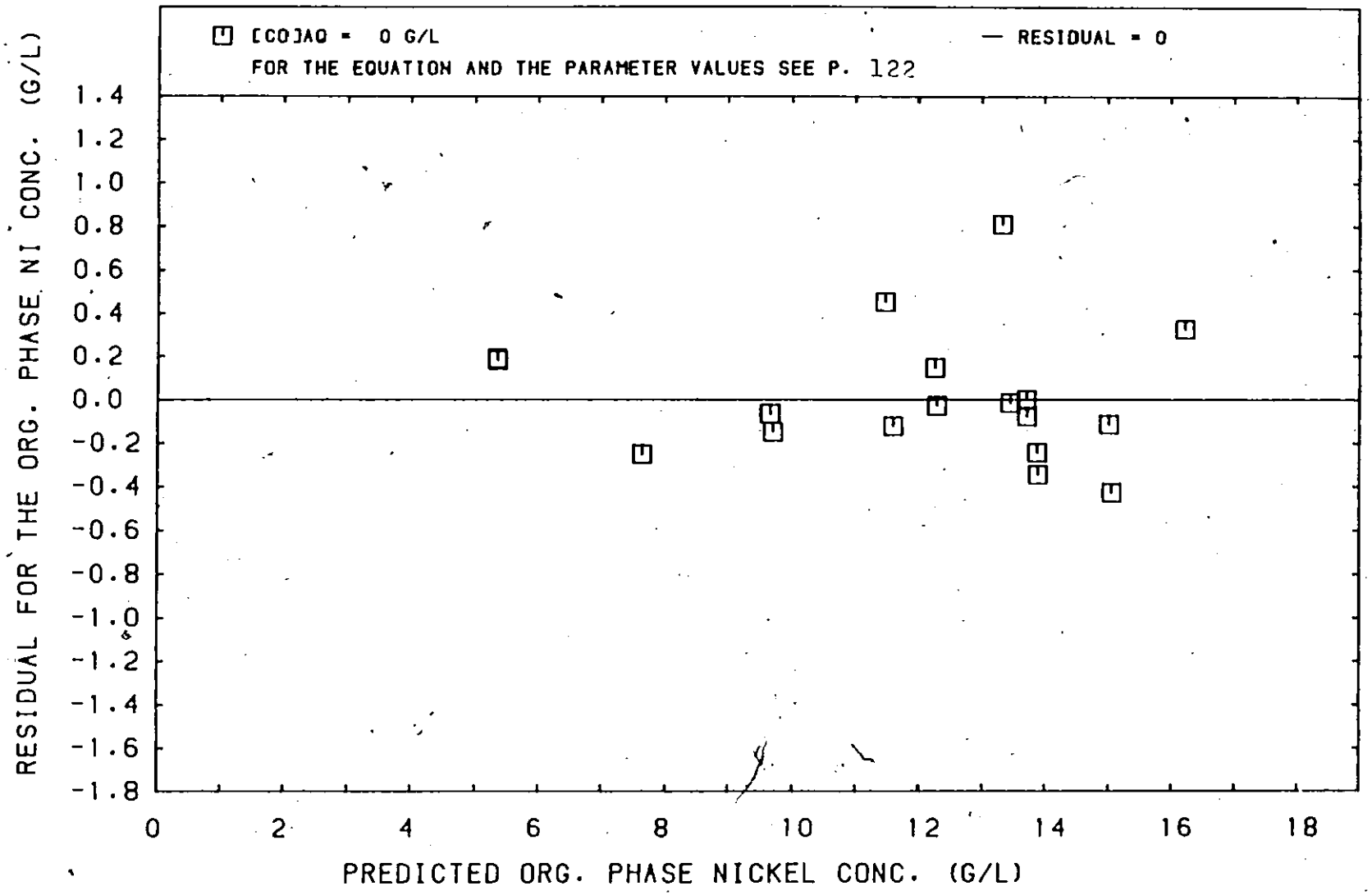


FIGURE 4C. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED PURE COMPONENT NICKEL EXTRACTION ISOTHERM AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 6.0-6.8.

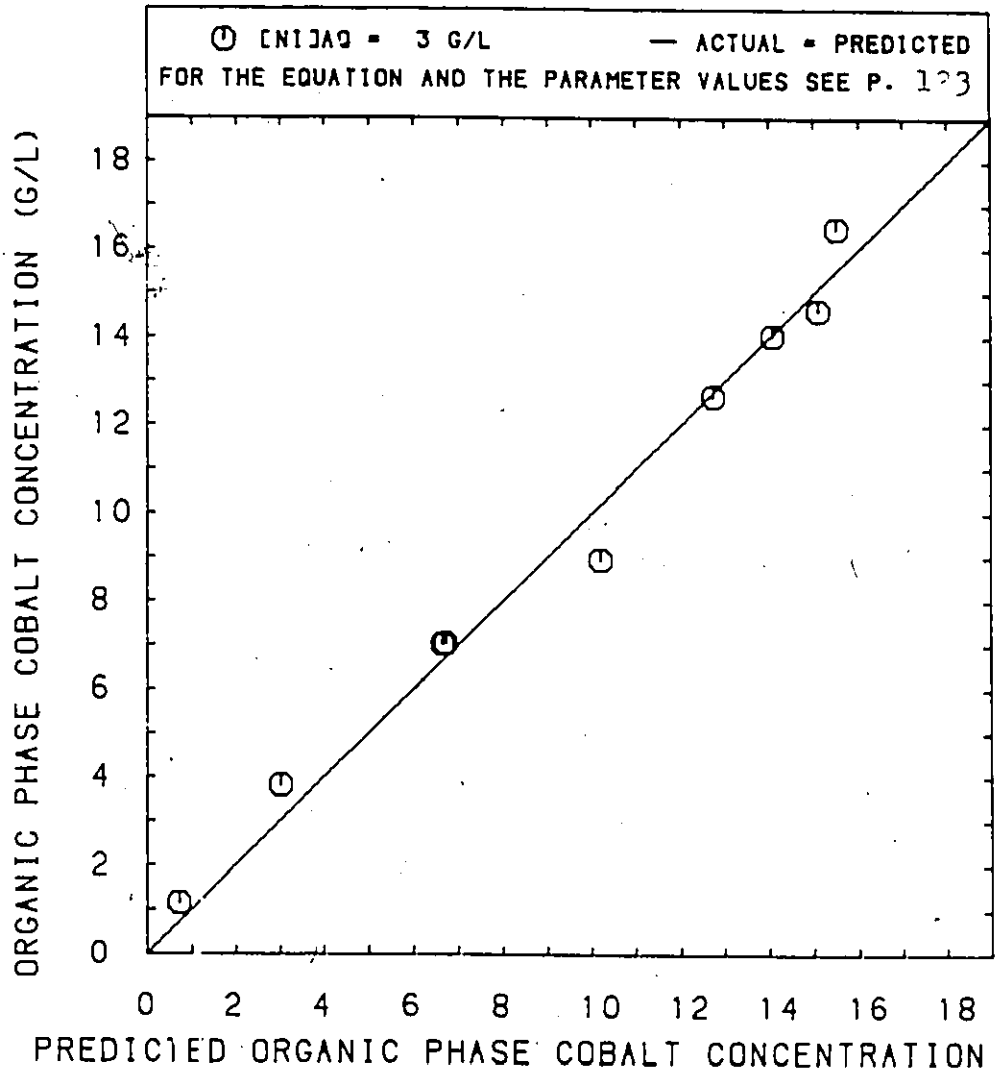


FIGURE 5A1. COMPARISON BETWEEN THE ACTUAL AND PREDICTED TWO COMPONENT COBALT EXTRACTION ISOTHERMS AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.3; A/O = 1.

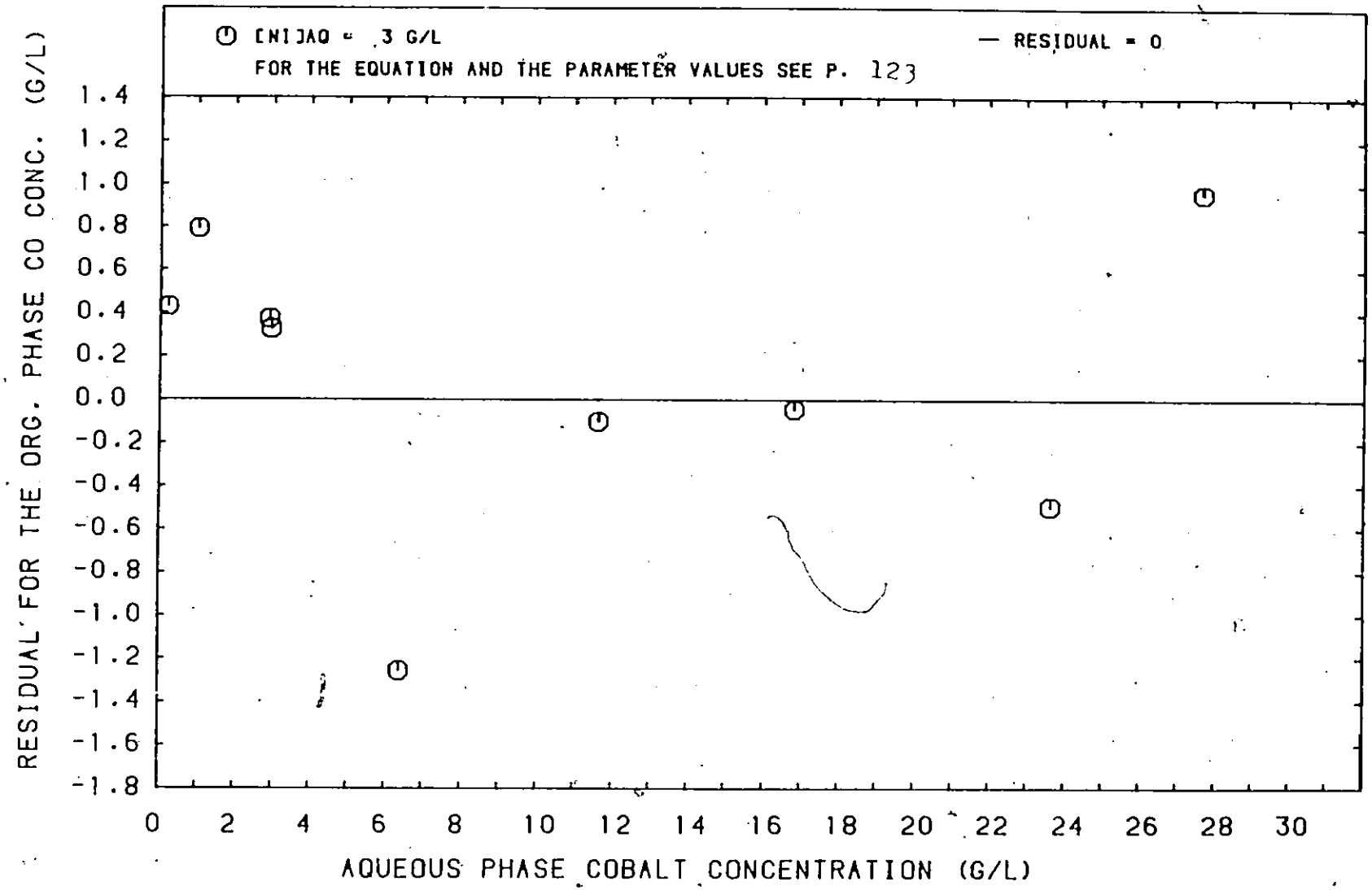


FIGURE 5B1. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE TWO COMPONENT COBALT EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.3.

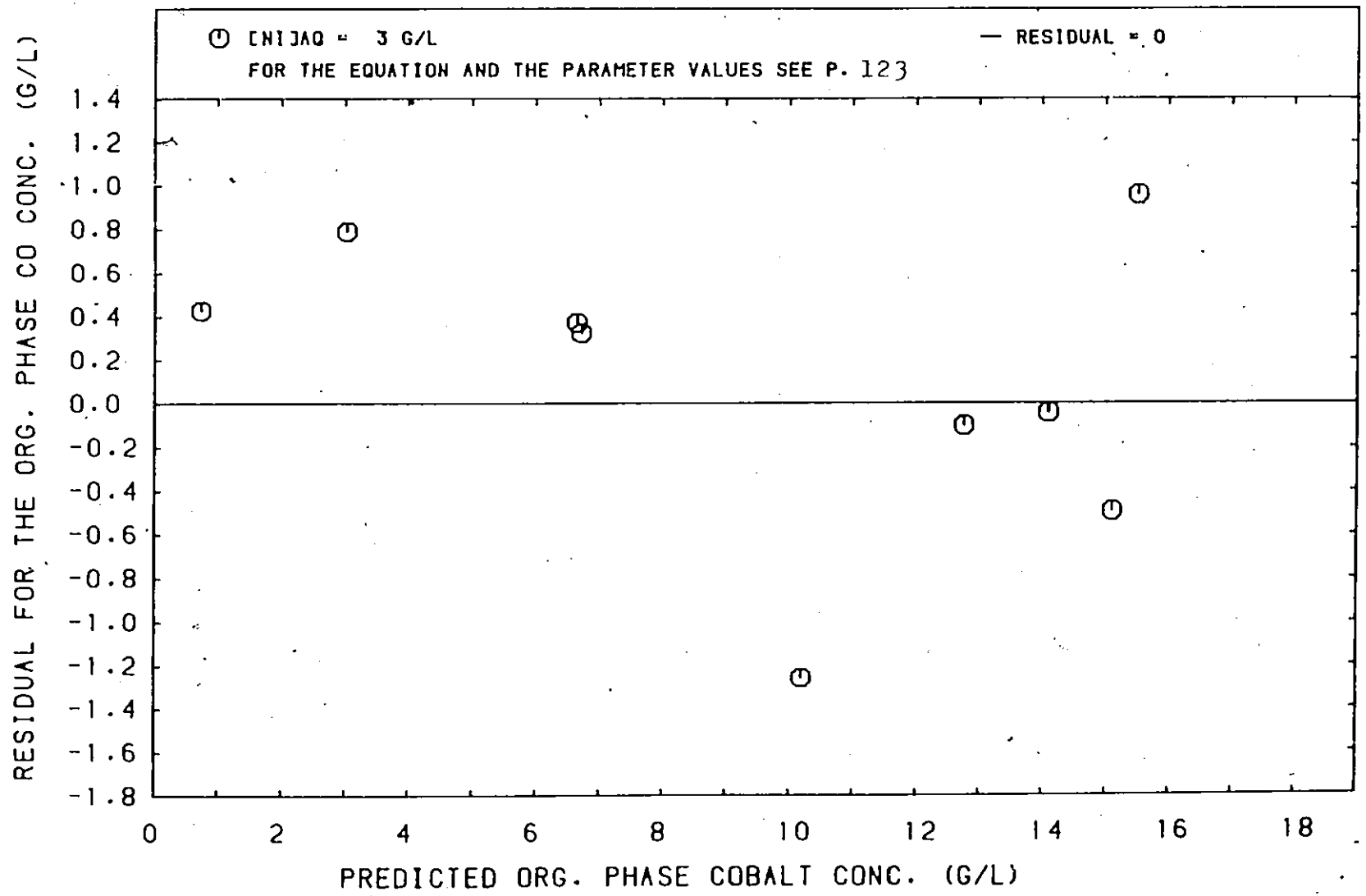


FIGURE 5C1. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED TWO COMPONENT COBALT EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.3.

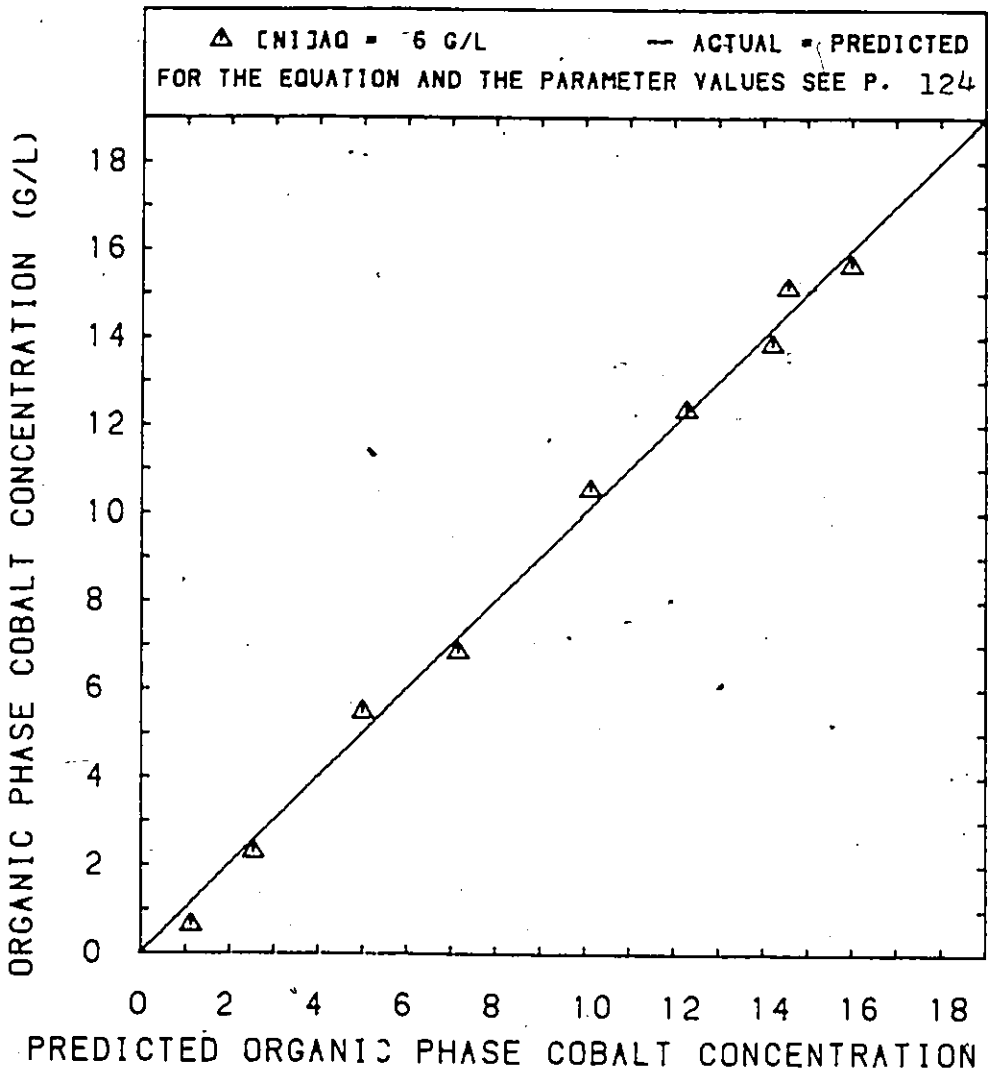


FIGURE 5A2. COMPARISON BETWEEN THE ACTUAL AND PREDICTED TWO COMPONENT COBALT EXTRACTION ISOTHERMS AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.3, A/O = 1.

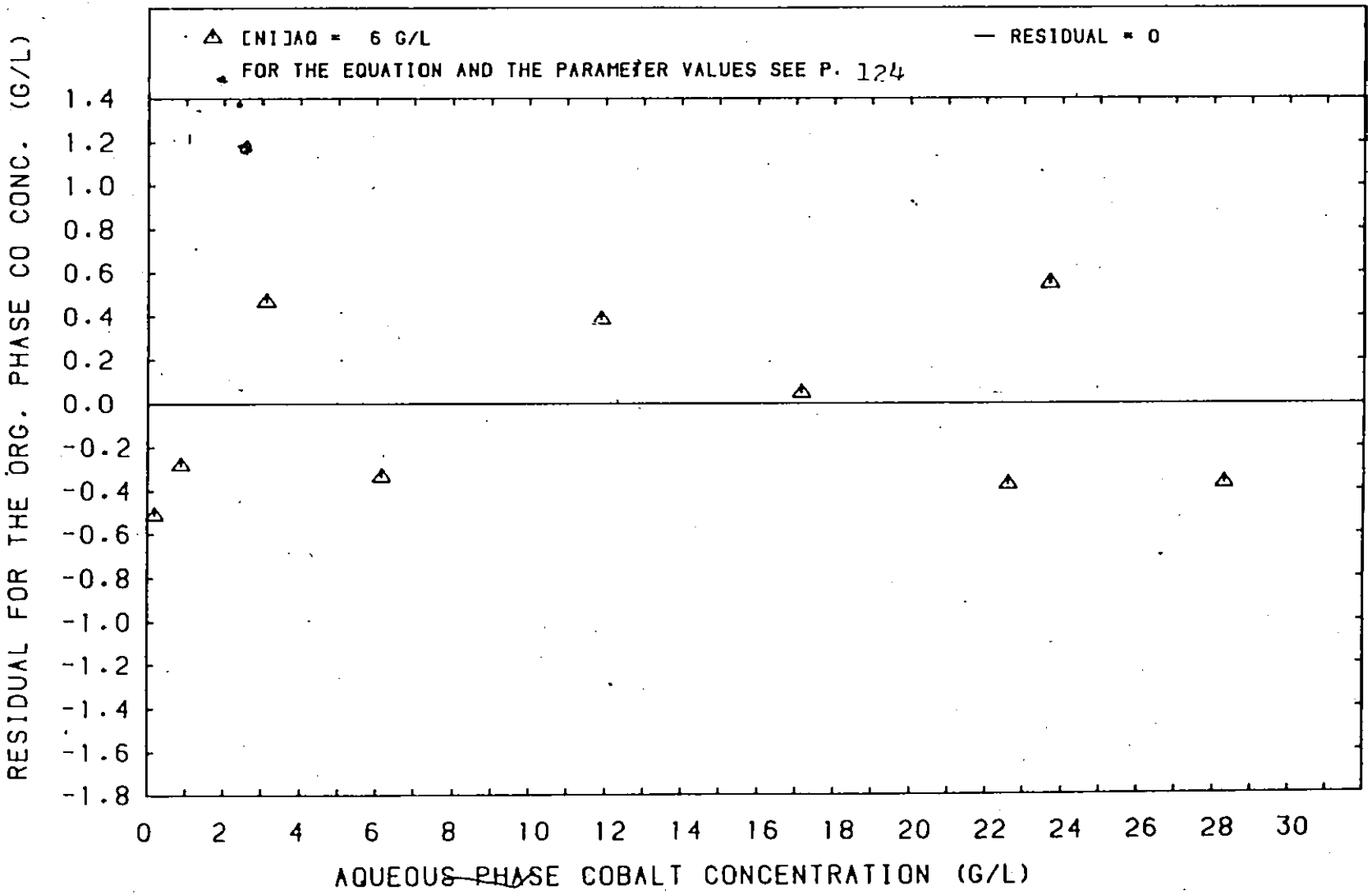


FIGURE 5B2. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE TWO COMPONENT COBALT EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.3.

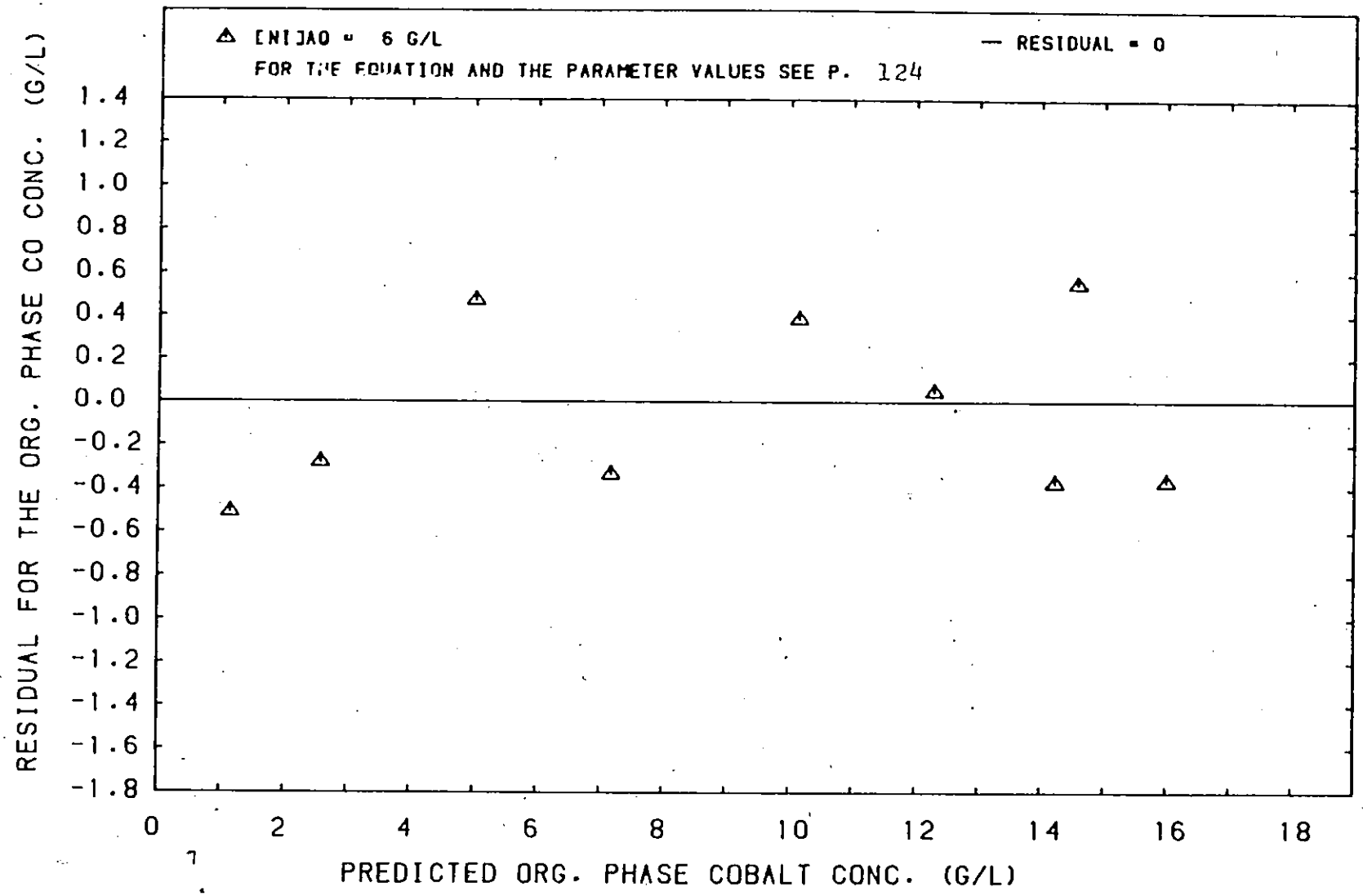


FIGURE 5C2. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED TWO COMPONENT COBALT EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.3.

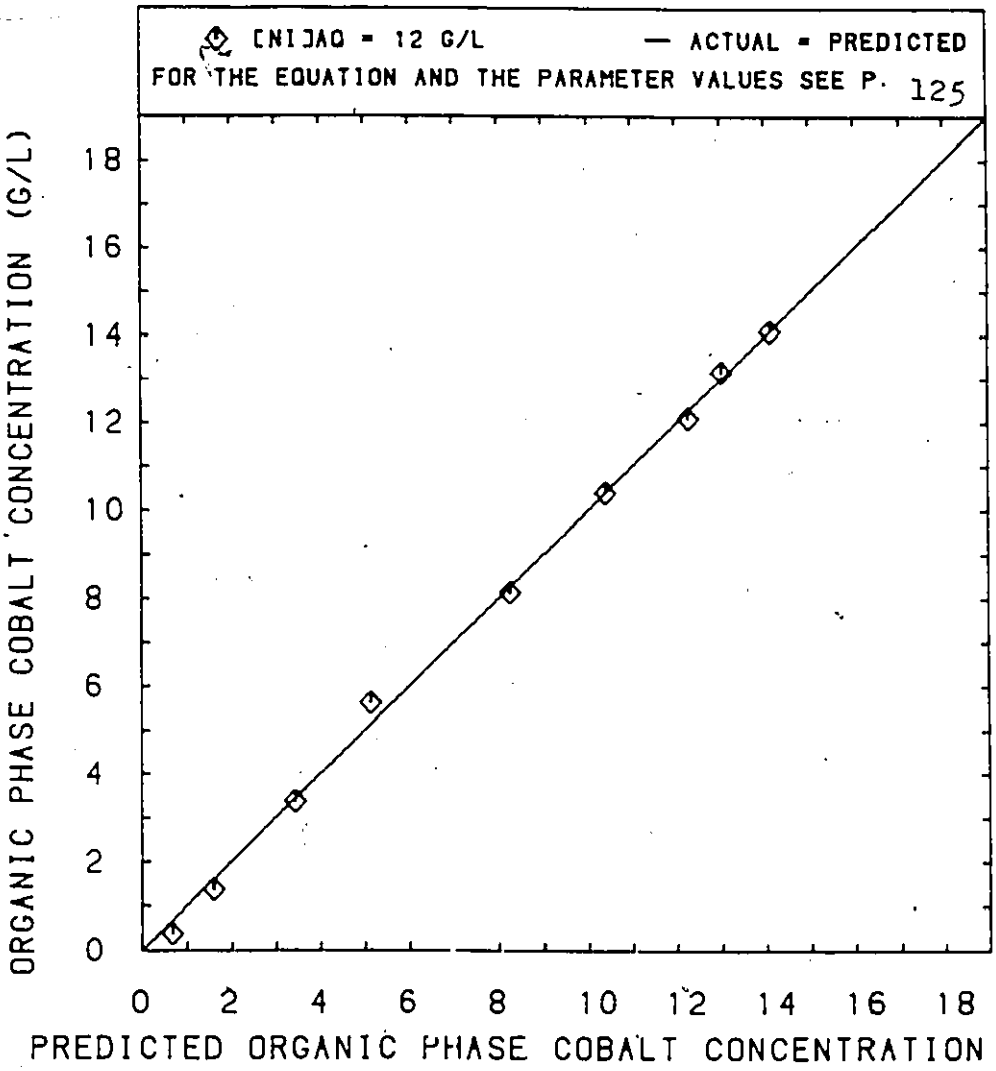


FIGURE 5A3. COMPARISON BETWEEN THE ACTUAL AND PREDICTED TWO COMPONENT COBALT EXTRACTION ISOTHERMS AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.3; A/O = 1.

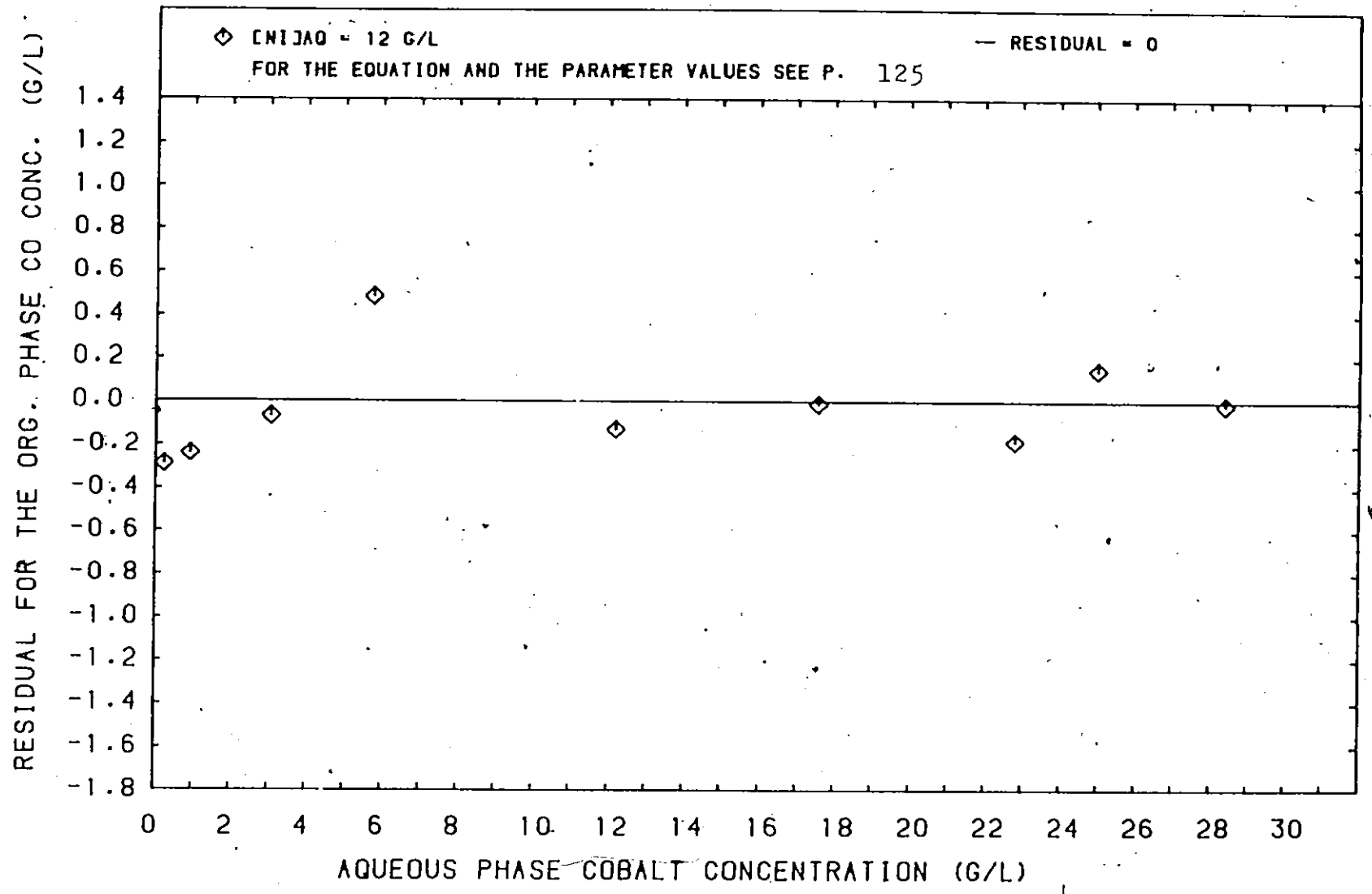


FIGURE 5B3. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE TWO COMPONENT COBALT EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.3.

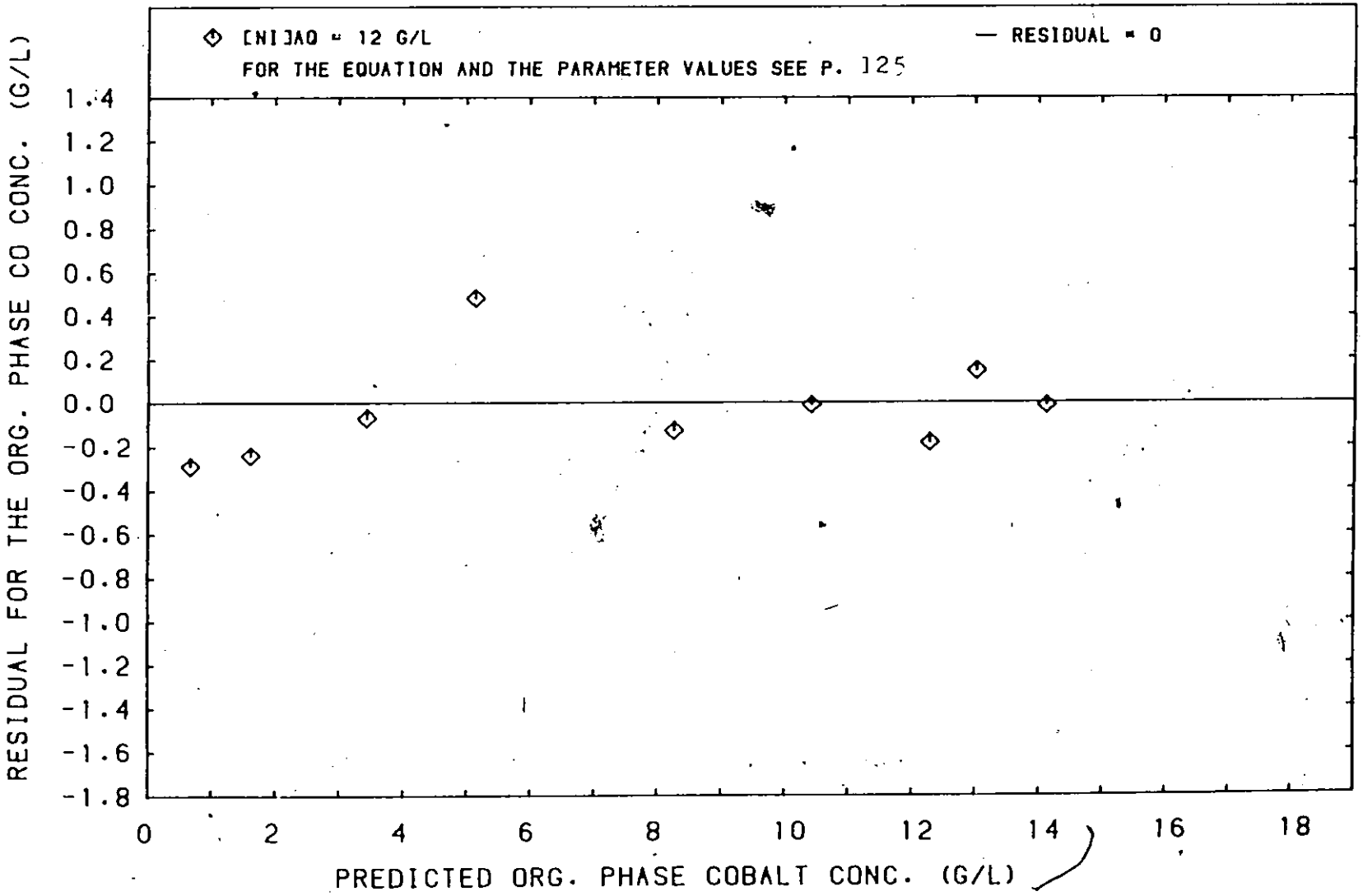


FIGURE 5C3. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED TWO COMPONENT COBALT EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.3.

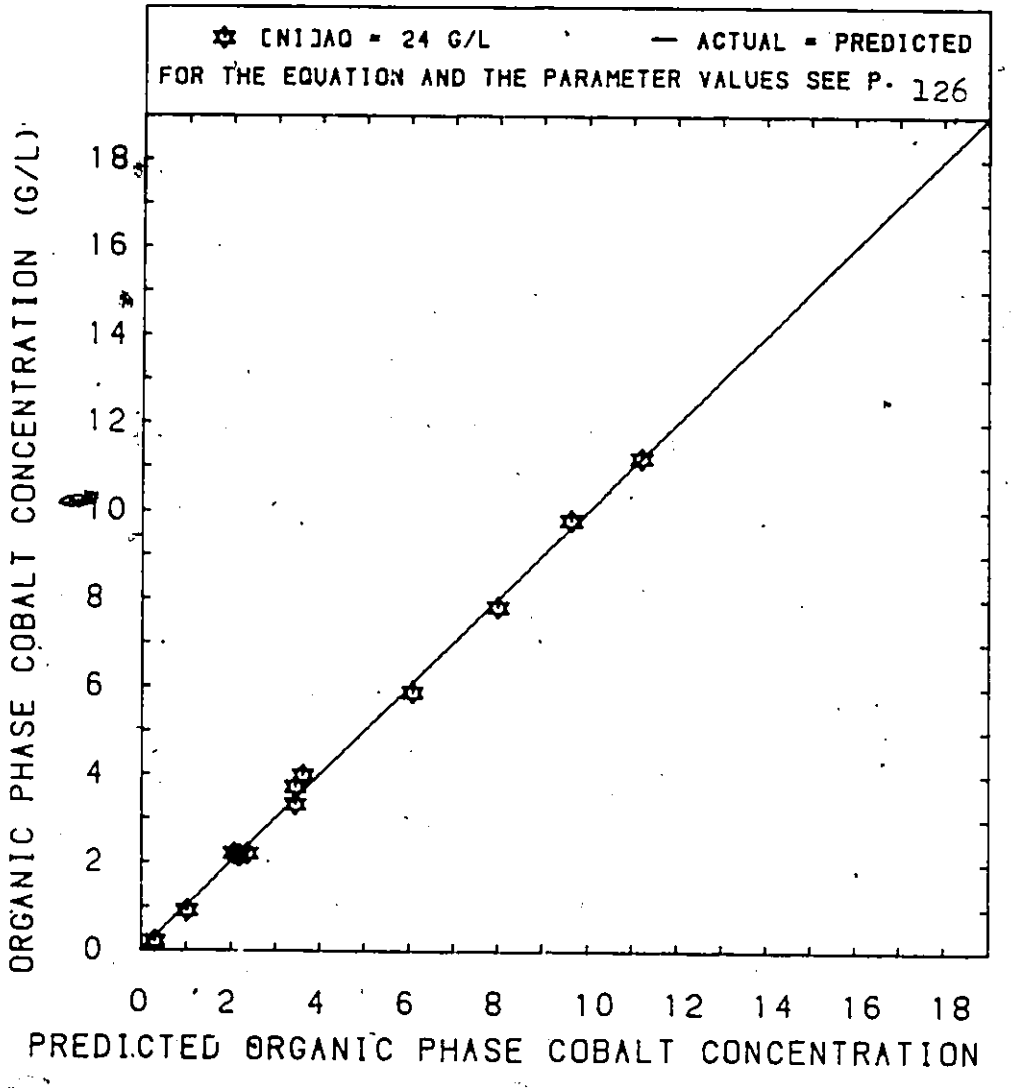


FIGURE 5A4. COMPARISON BETWEEN THE ACTUAL AND PREDICTED TWO COMPONENT COBALT EXTRACTION ISOTHERMS AT 25 DEG. C.
ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.3; A/O = 1.

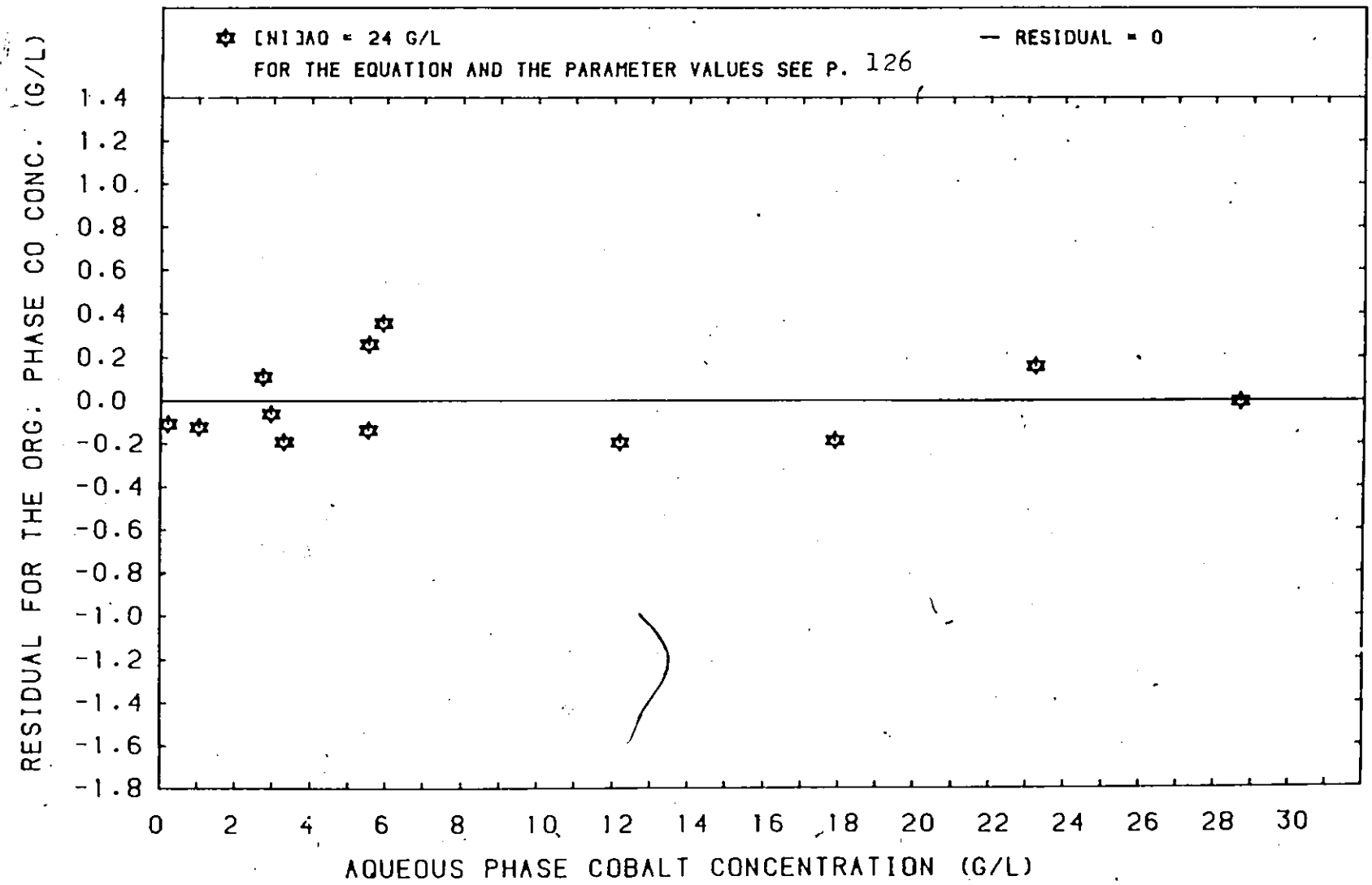


FIGURE 534. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE TWO COMPONENT COBALT EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.3.

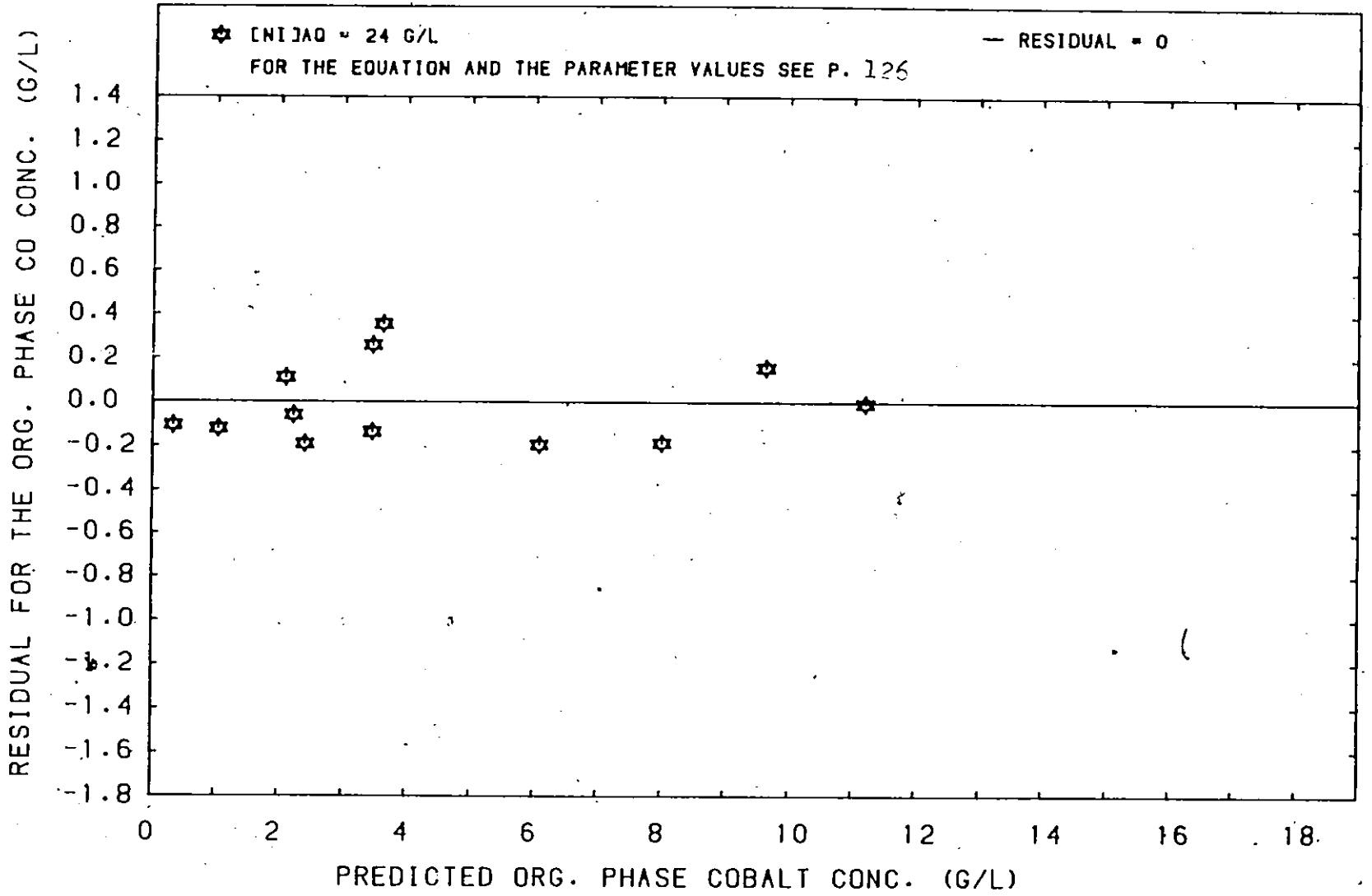


FIGURE 5C4. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED TWO COMPONENT COBALT EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.3.

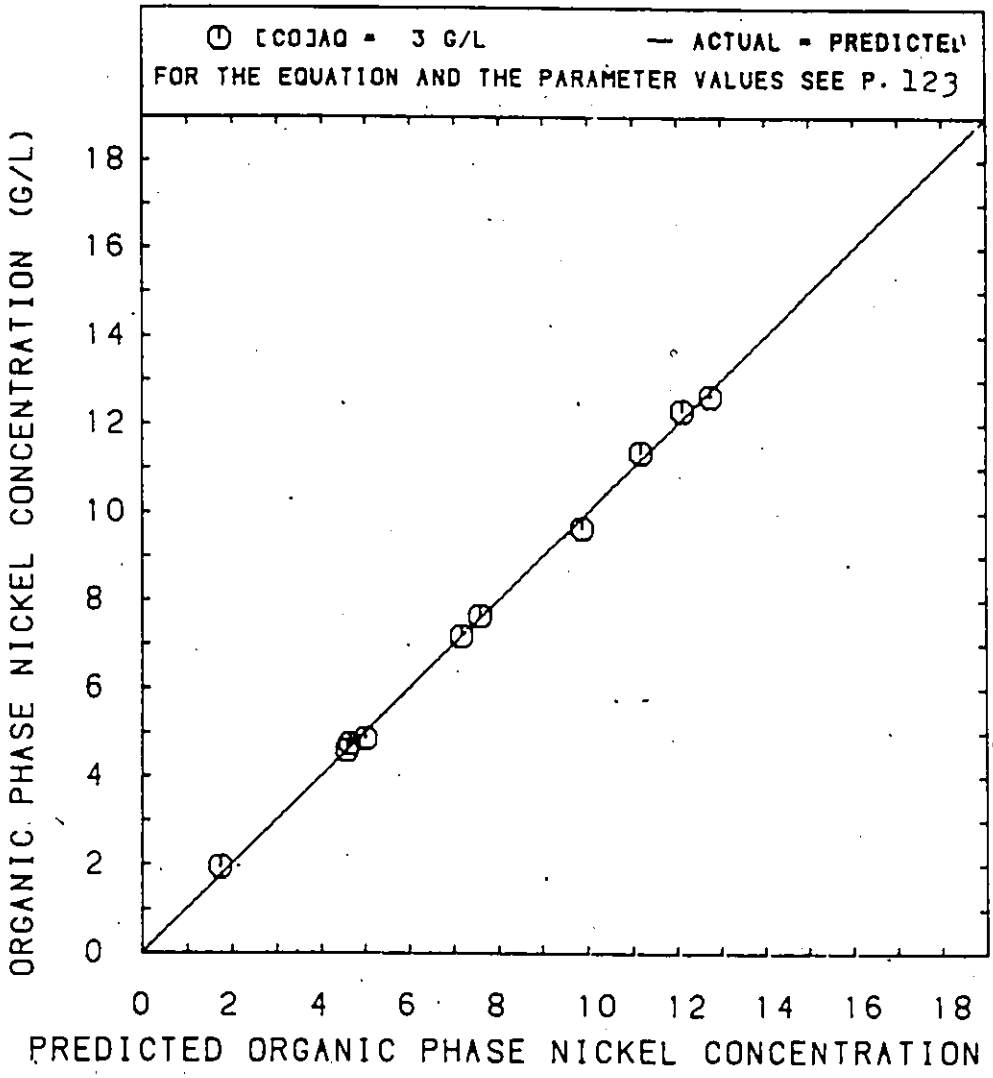


FIGURE 6A1. COMPARISON BETWEEN THE ACTUAL AND PREDICTED TWO COMPONENT NICKEL EXTRACTION ISOTHERMS AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.4; A/O = 1.

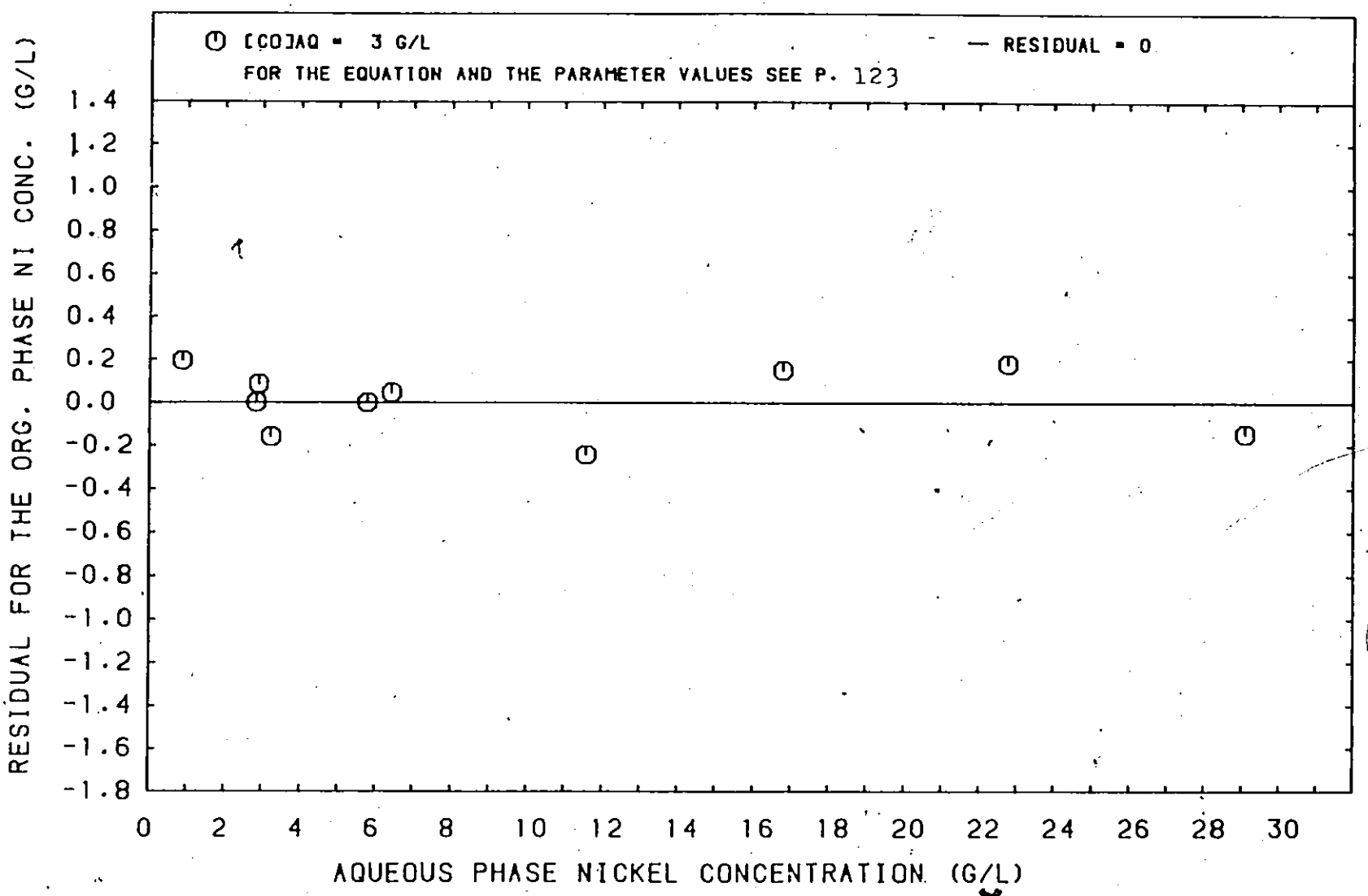


FIGURE 6B1. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE TWO COMPONENT NICKEL EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

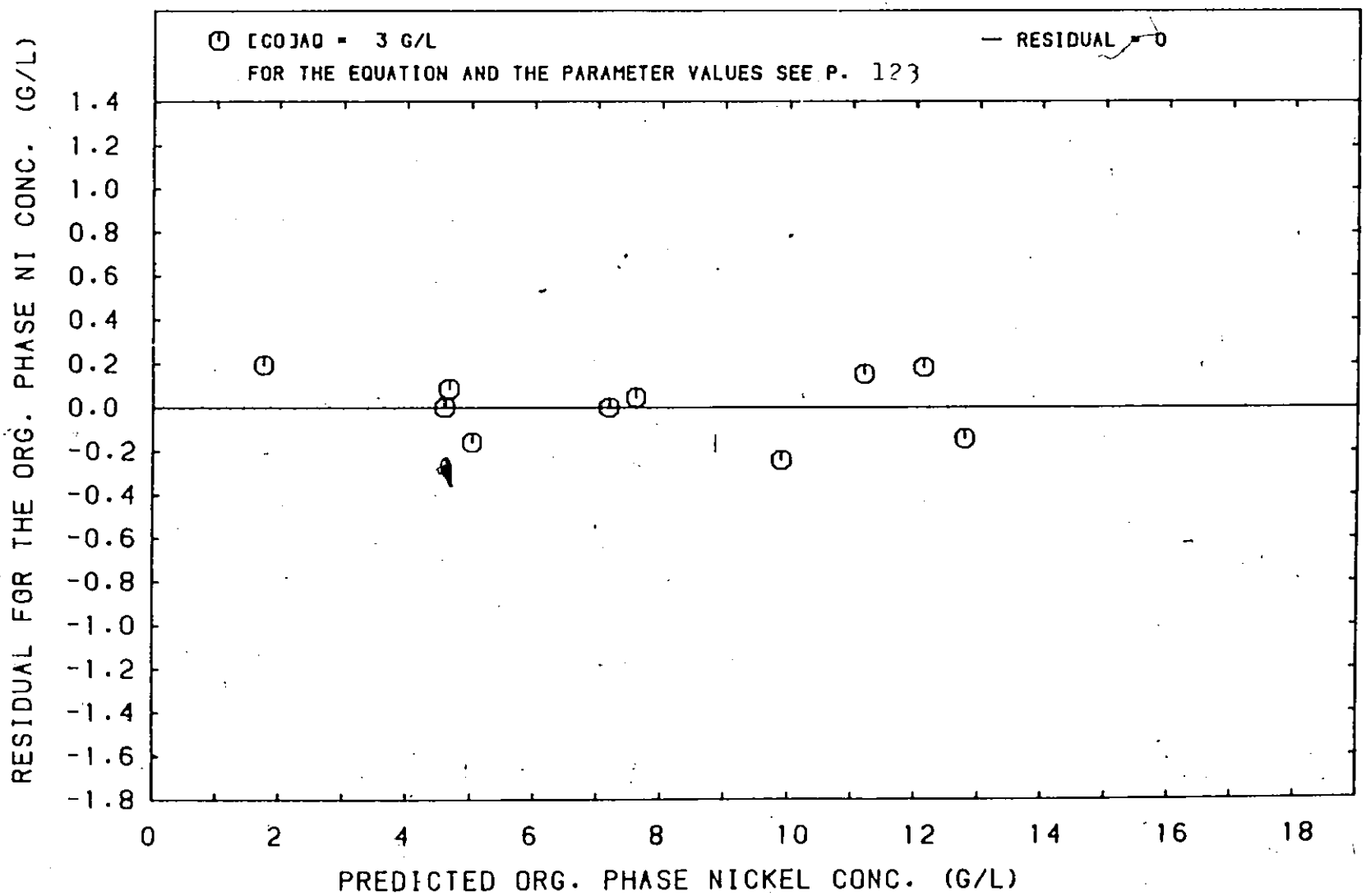


FIGURE 6C1. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED TWO COMPONENT NICKEL EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

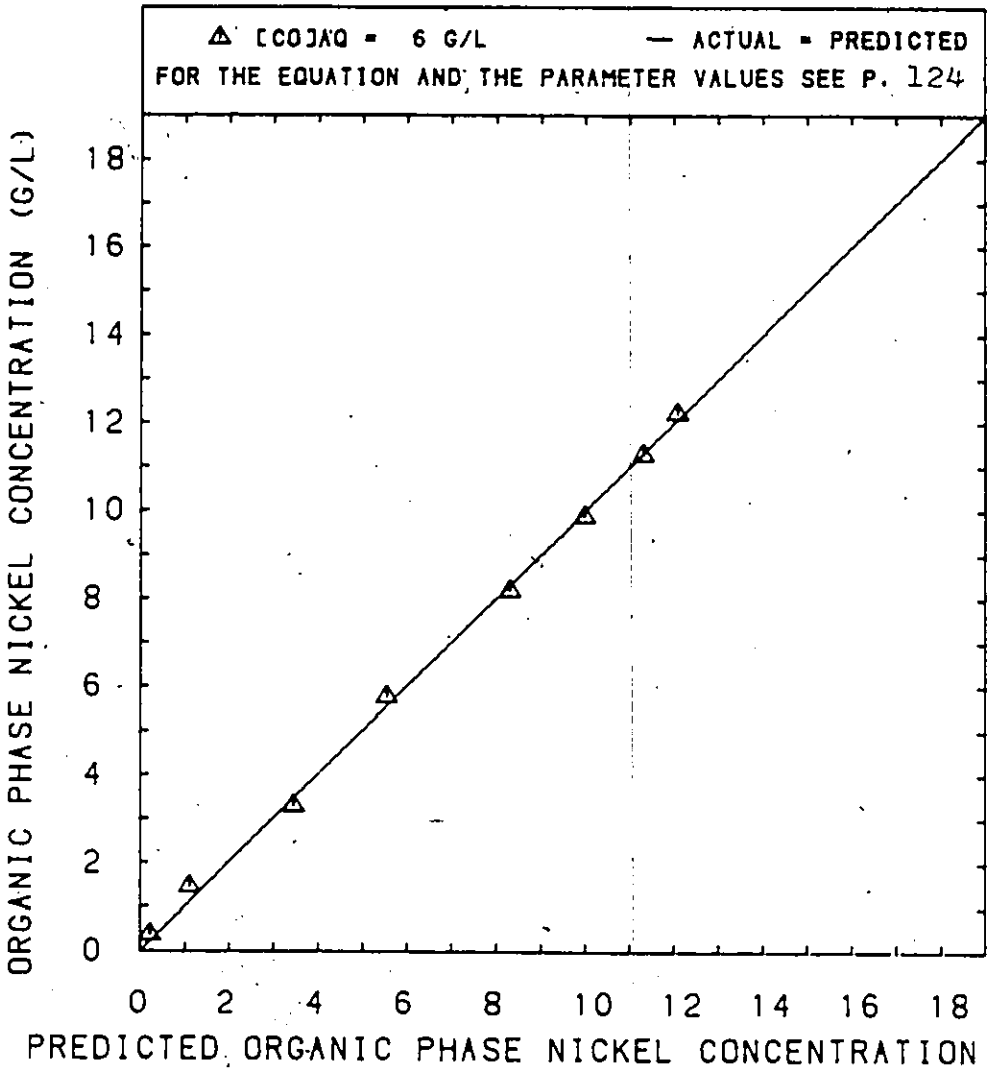


FIGURE 6A2. COMPARISON BETWEEN THE ACTUAL AND PREDICTED TWO COMPONENT NICKEL EXTRACTION ISOTHERMS AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.4; A/O = 1.

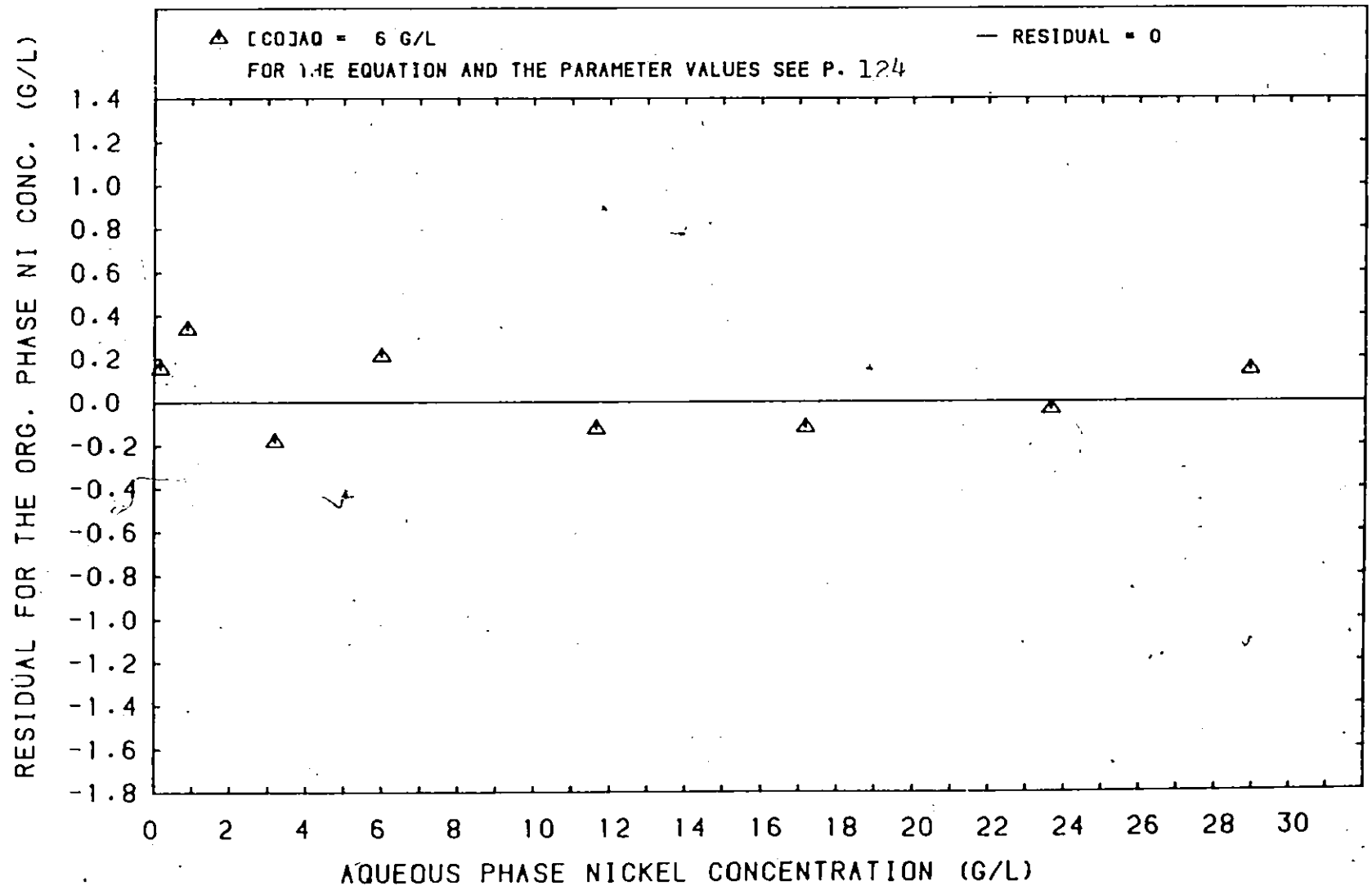


FIGURE 6B2. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE TWO COMPONENT NICKEL EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

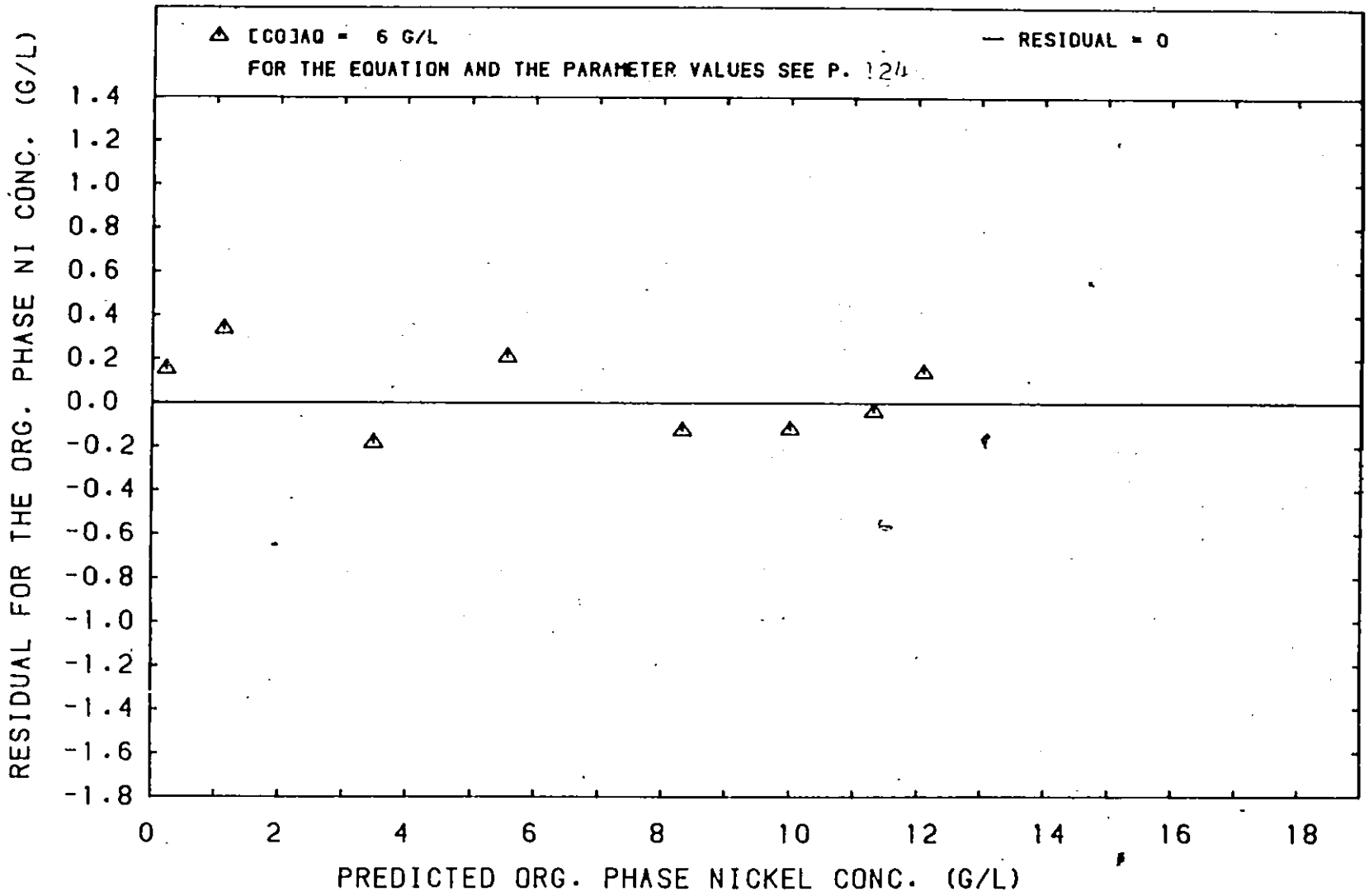


FIGURE 6C2. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED TWO COMPONENT NICKEL EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

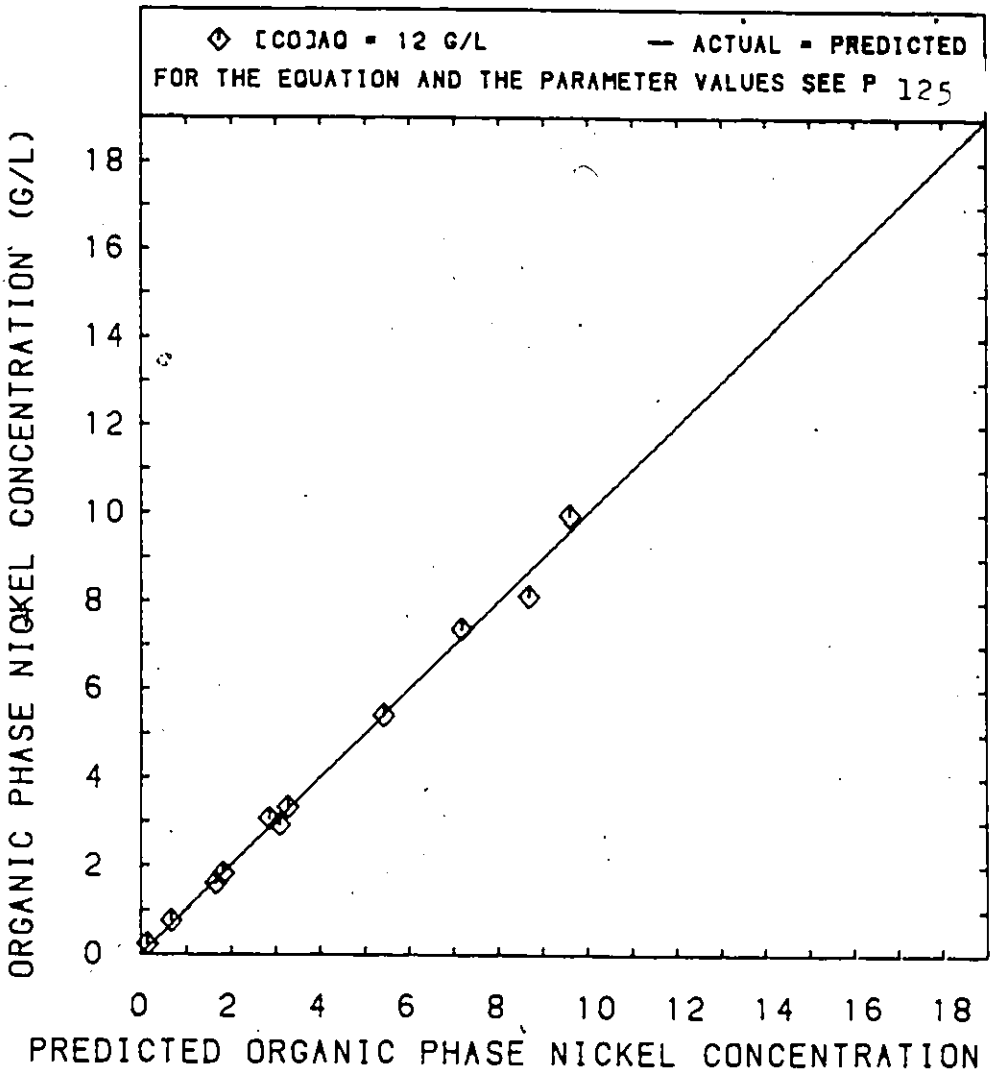


FIGURE 6A3. COMPARISON BETWEEN THE ACTUAL AND PREDICTED TWO COMPONENT NICKEL EXTRACTION ISOTHERMS AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.4; A/O = 1.

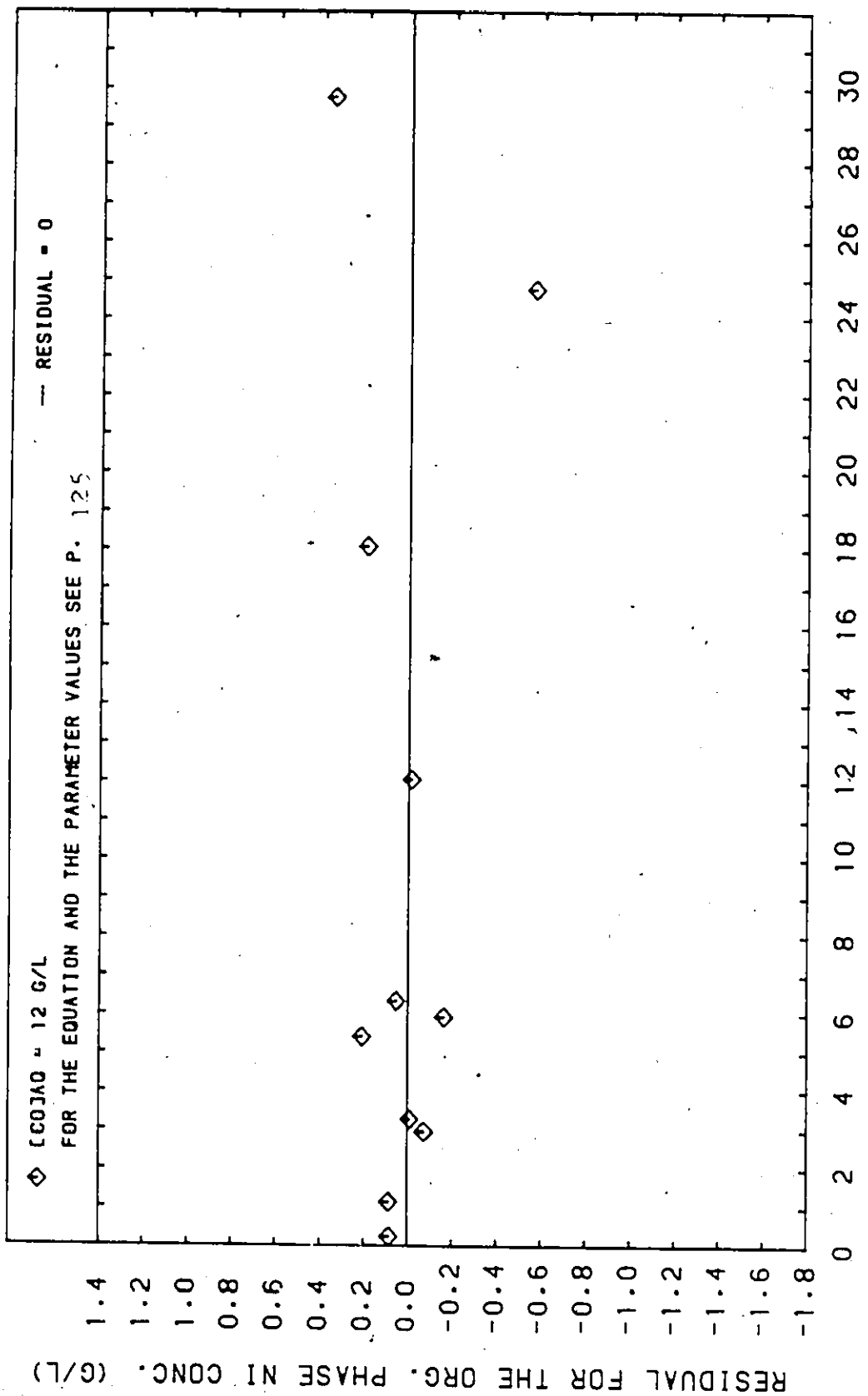


FIGURE 6B3.RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE TWO COMPONENT NICKEL EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

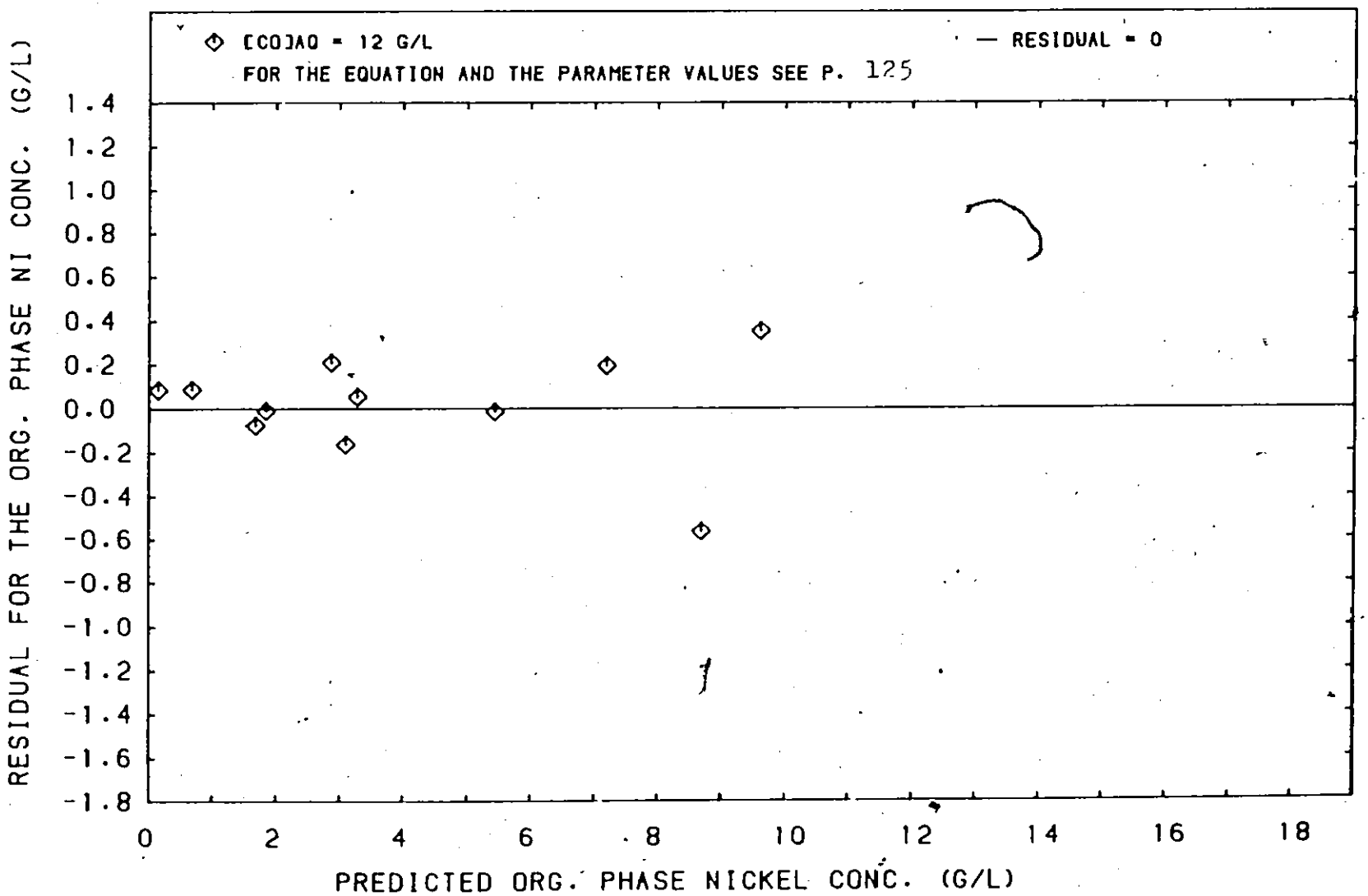


FIGURE 6C3. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED TWO COMPONENT NICKEL EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

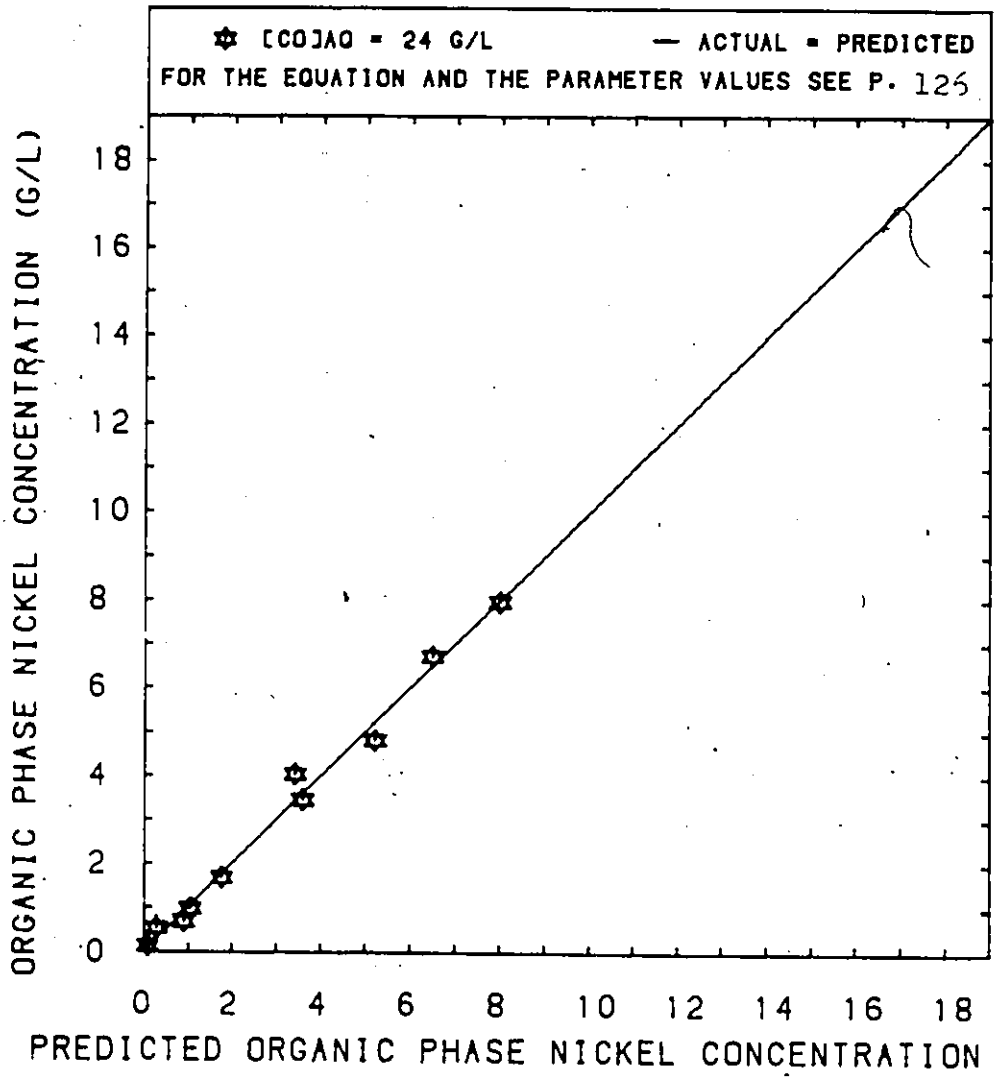


FIGURE 6A4. COMPARISON BETWEEN THE ACTUAL AND PREDICTED TWO COMPONENT NICKEL EXTRACTION ISOTHERMS AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.4; A/O = 1.

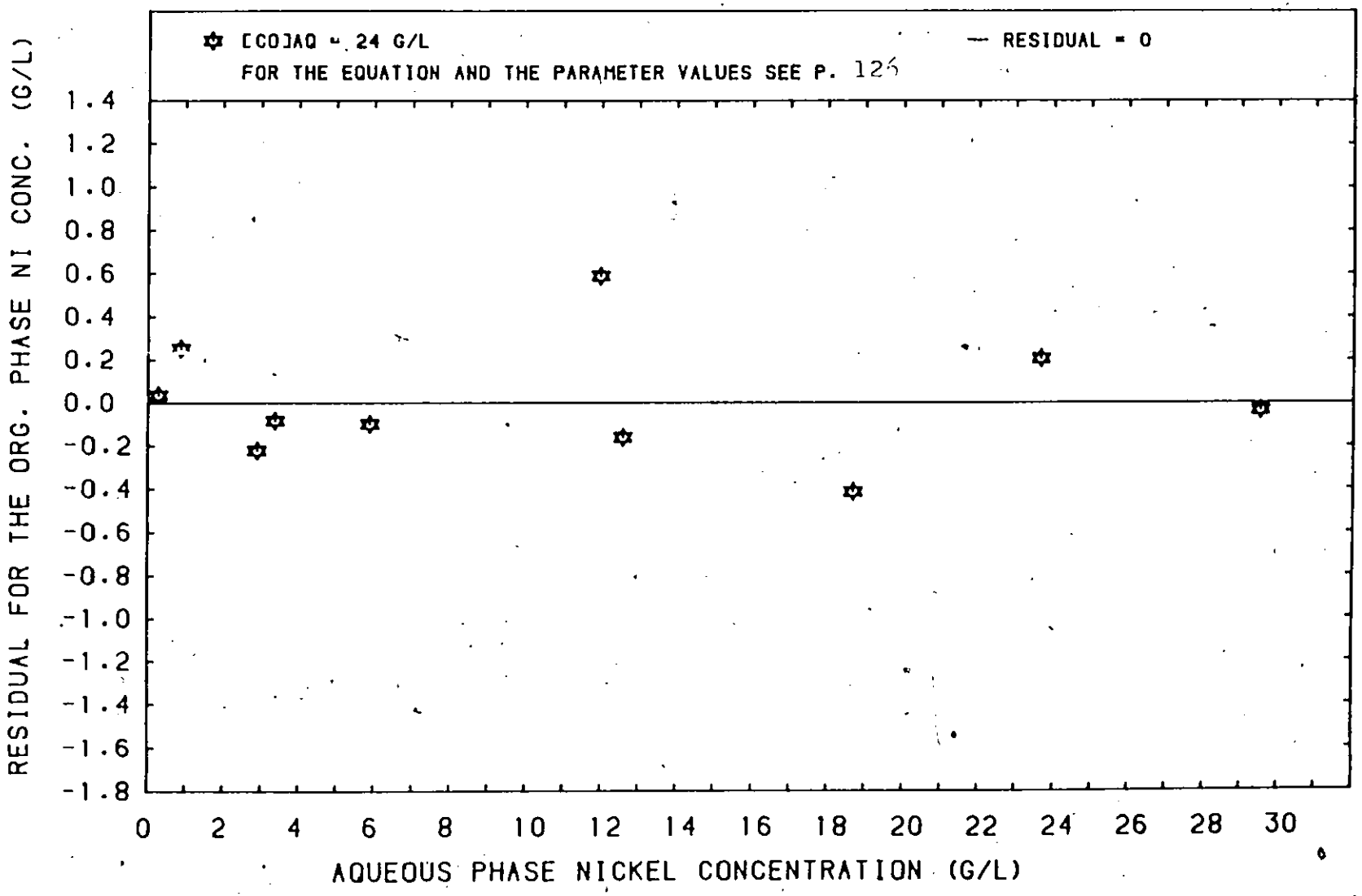


FIGURE 6B4. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE METAL CONC. FOR THE TWO COMPONENT NICKEL EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

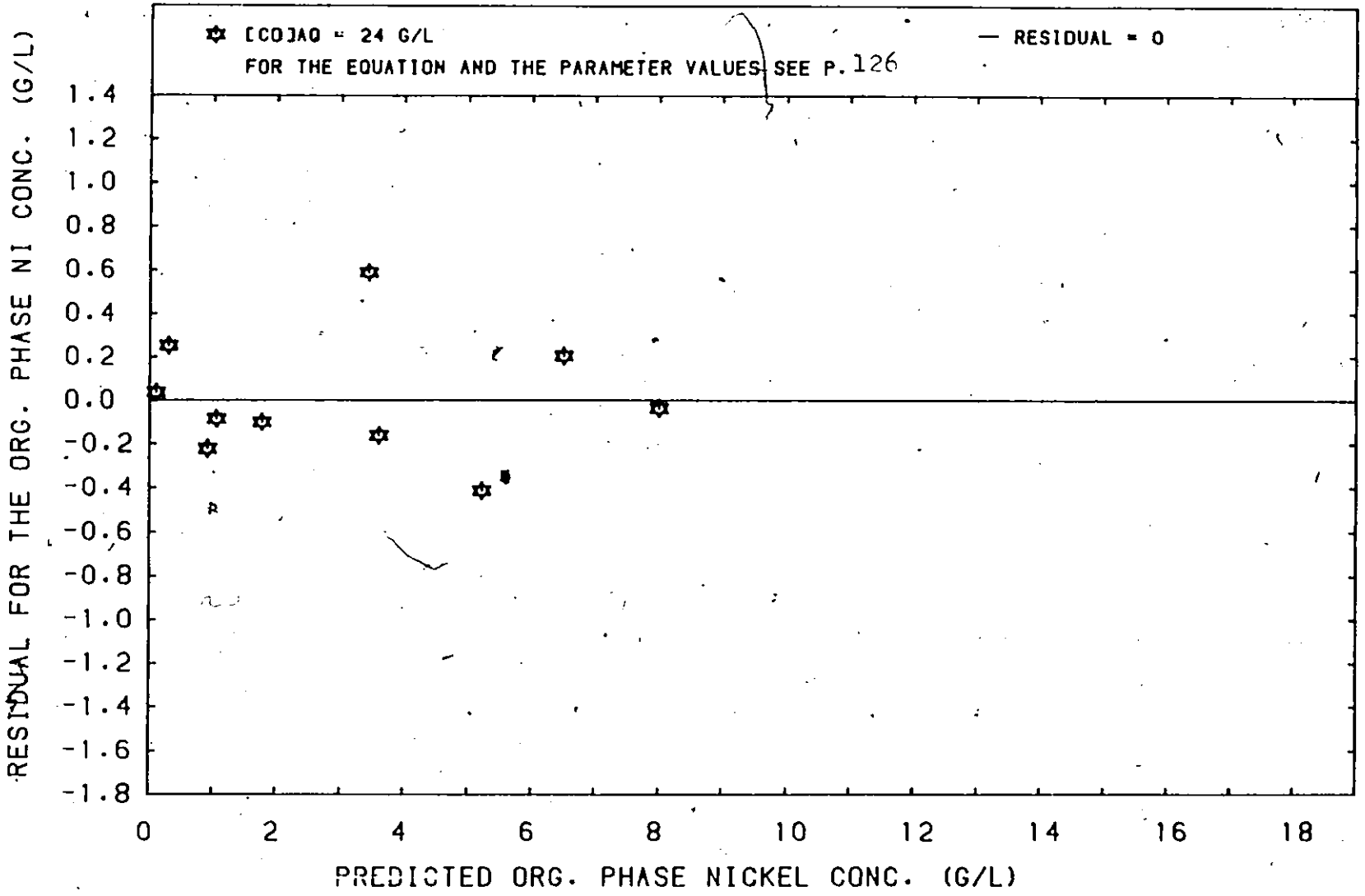


FIGURE 6.4. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED TWO COMPONENT NICKEL EXTRACTION ISOTHERM AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

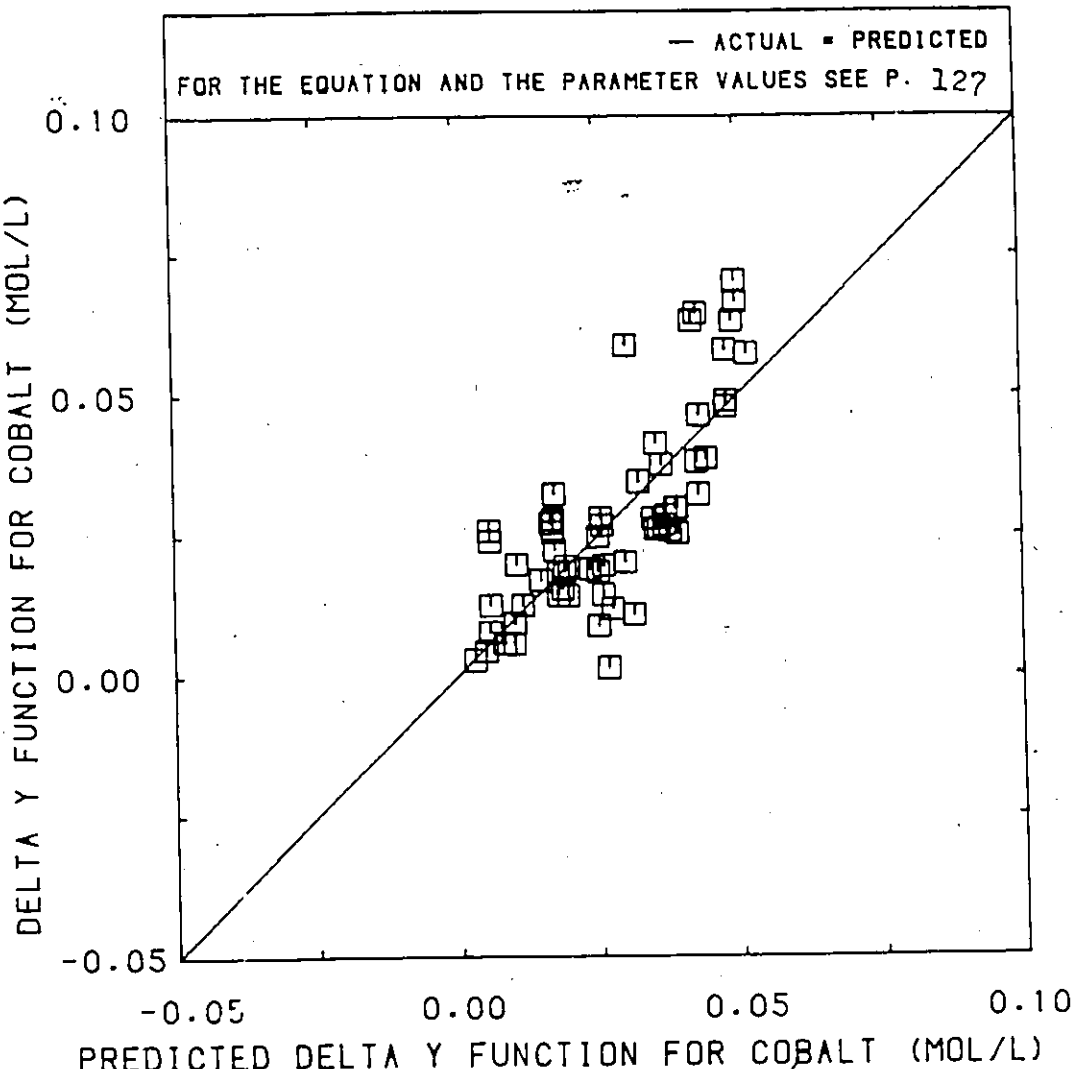


FIGURE 9A. COMPARISON BETWEEN THE ACTUAL AND PREDICTED DELTA Y FUNCTIONS FOR COBALT AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.3; A/O = 1.

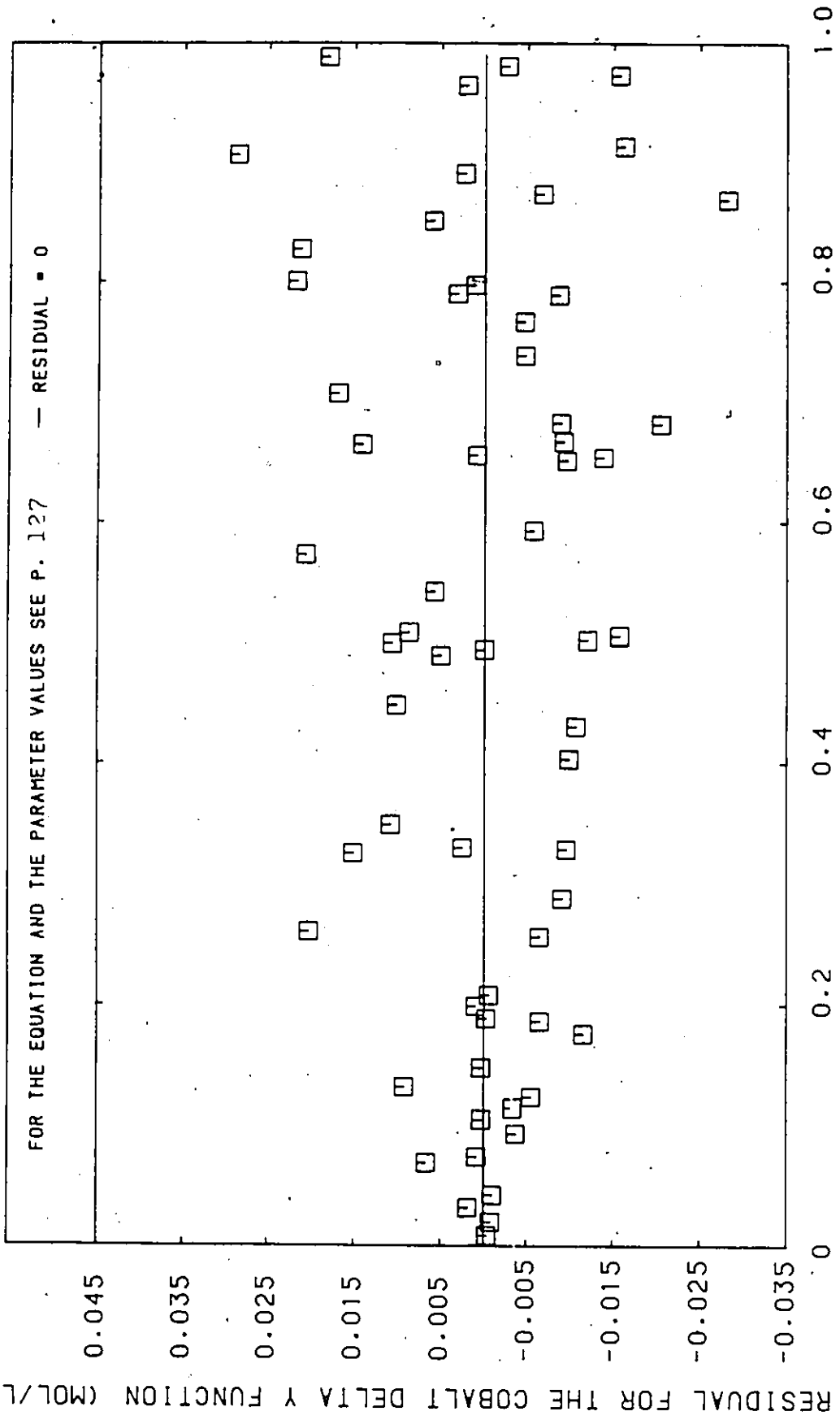


FIGURE 9B. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE COBALT MOLE FRACTION FOR THE COBALT DELTA Y FUNCTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.3.

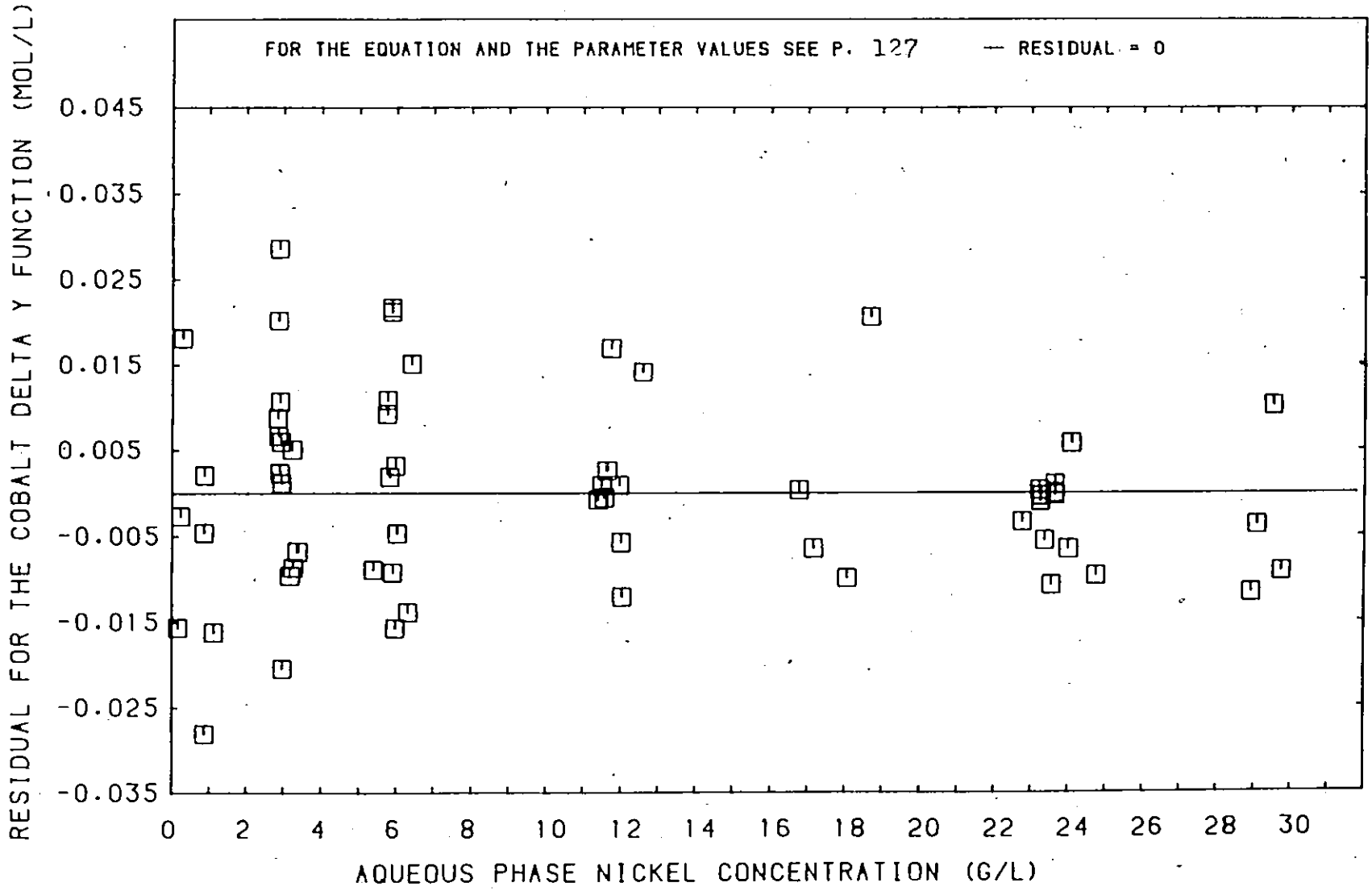


FIGURE 9C. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE NICKEL CONC. FOR THE COBALT DELTA Y FUNCTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.3.

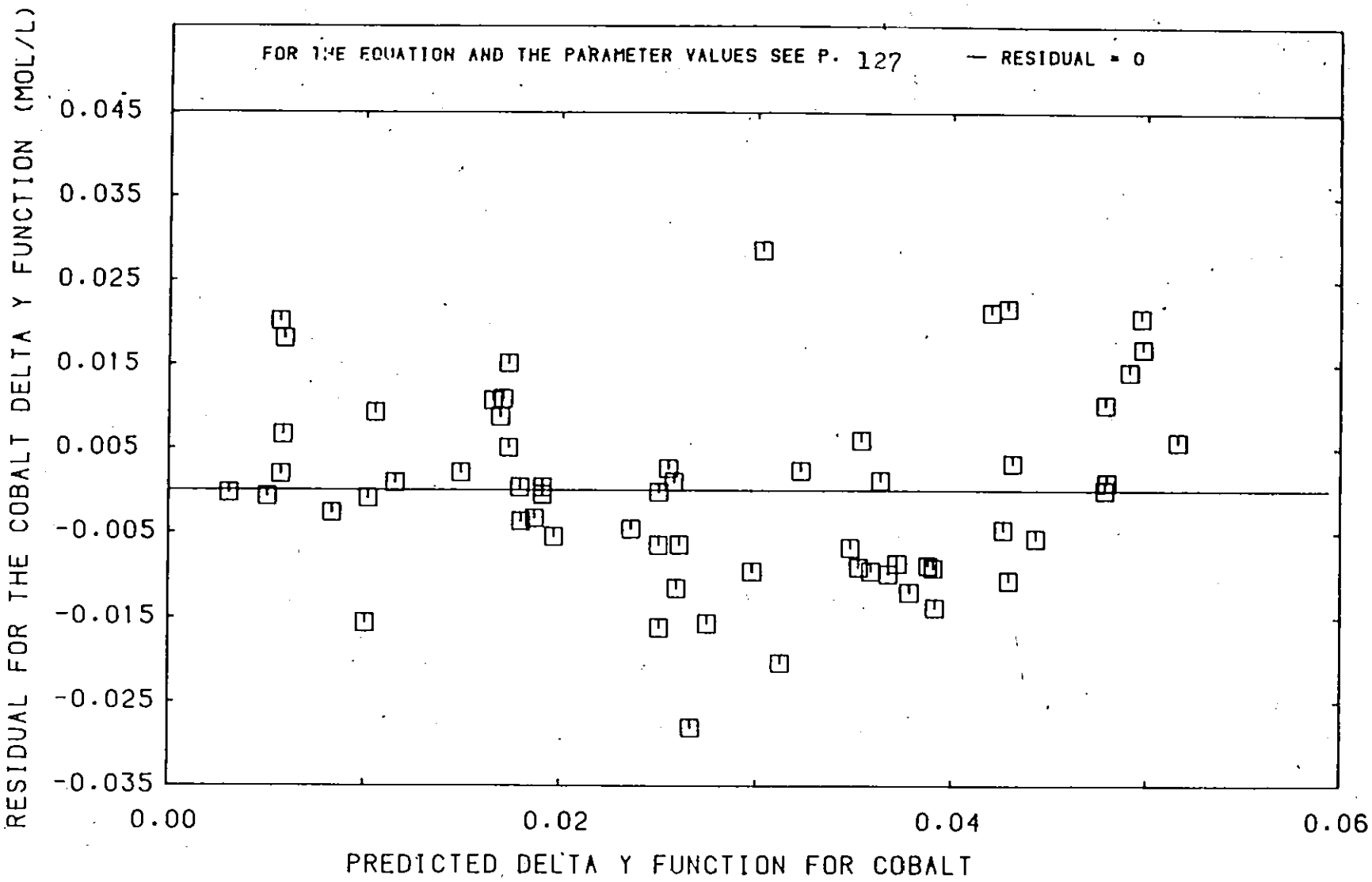


FIGURE 9D. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED COBALT DELTA Y FUNCTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.3.

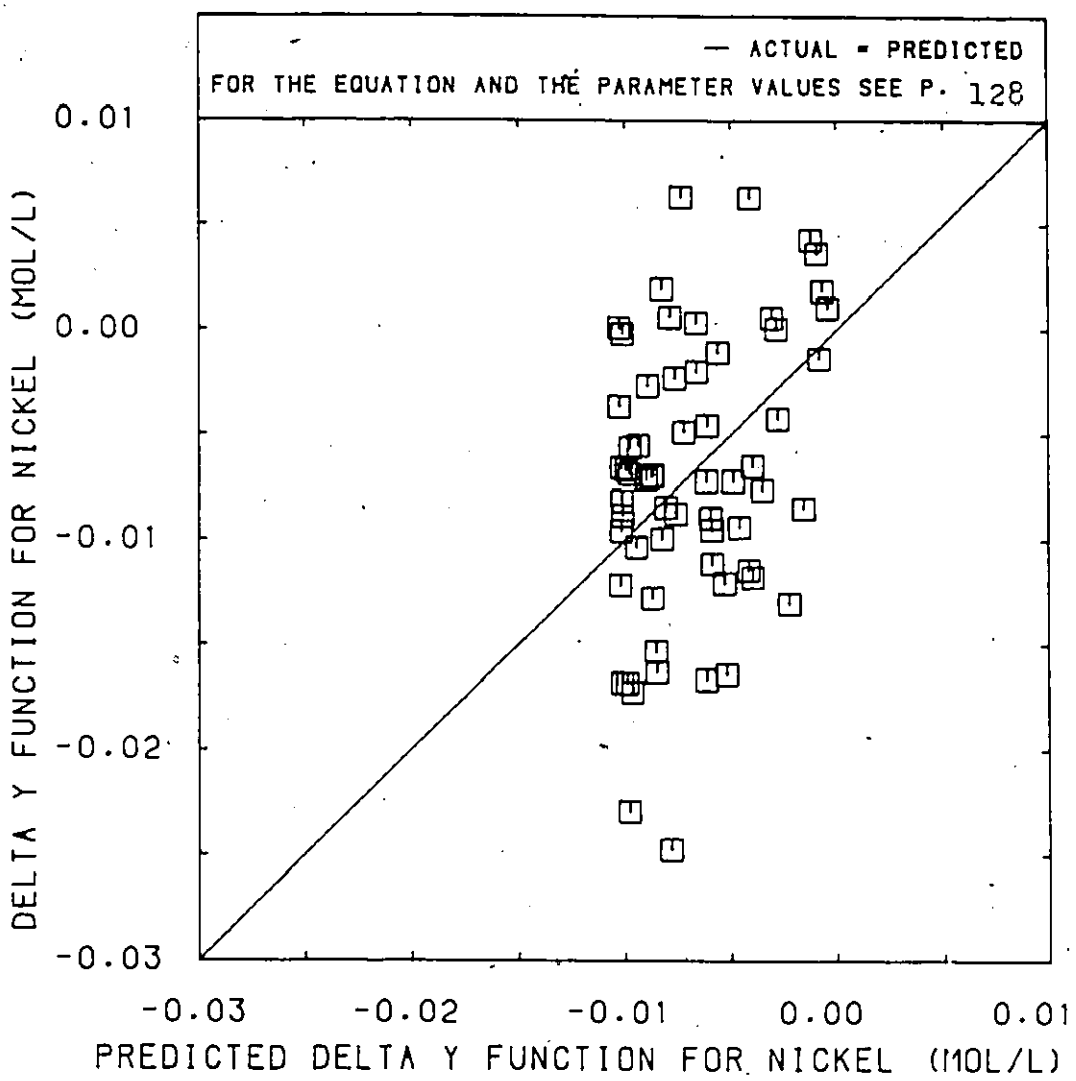


FIGURE 10A. COMPARISON BETWEEN THE ACTUAL AND PREDICTED DELTA Y FUNCTIONS FOR NICKEL AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3541, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.4; A/O = 1.

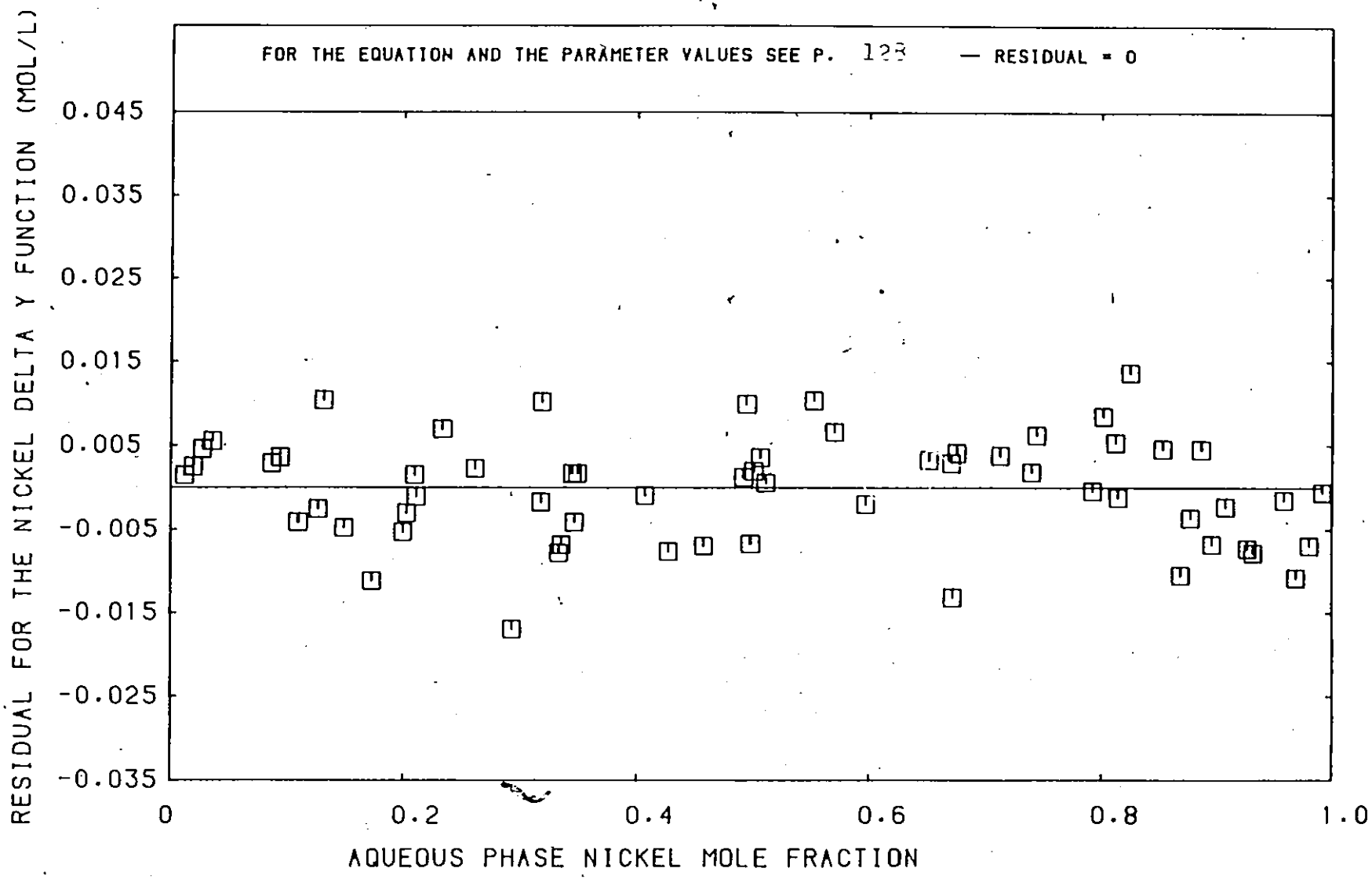


FIGURE 10B. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE NICKEL MOLE FRACTION FOR THE NICKEL DELTA Y FUNCTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

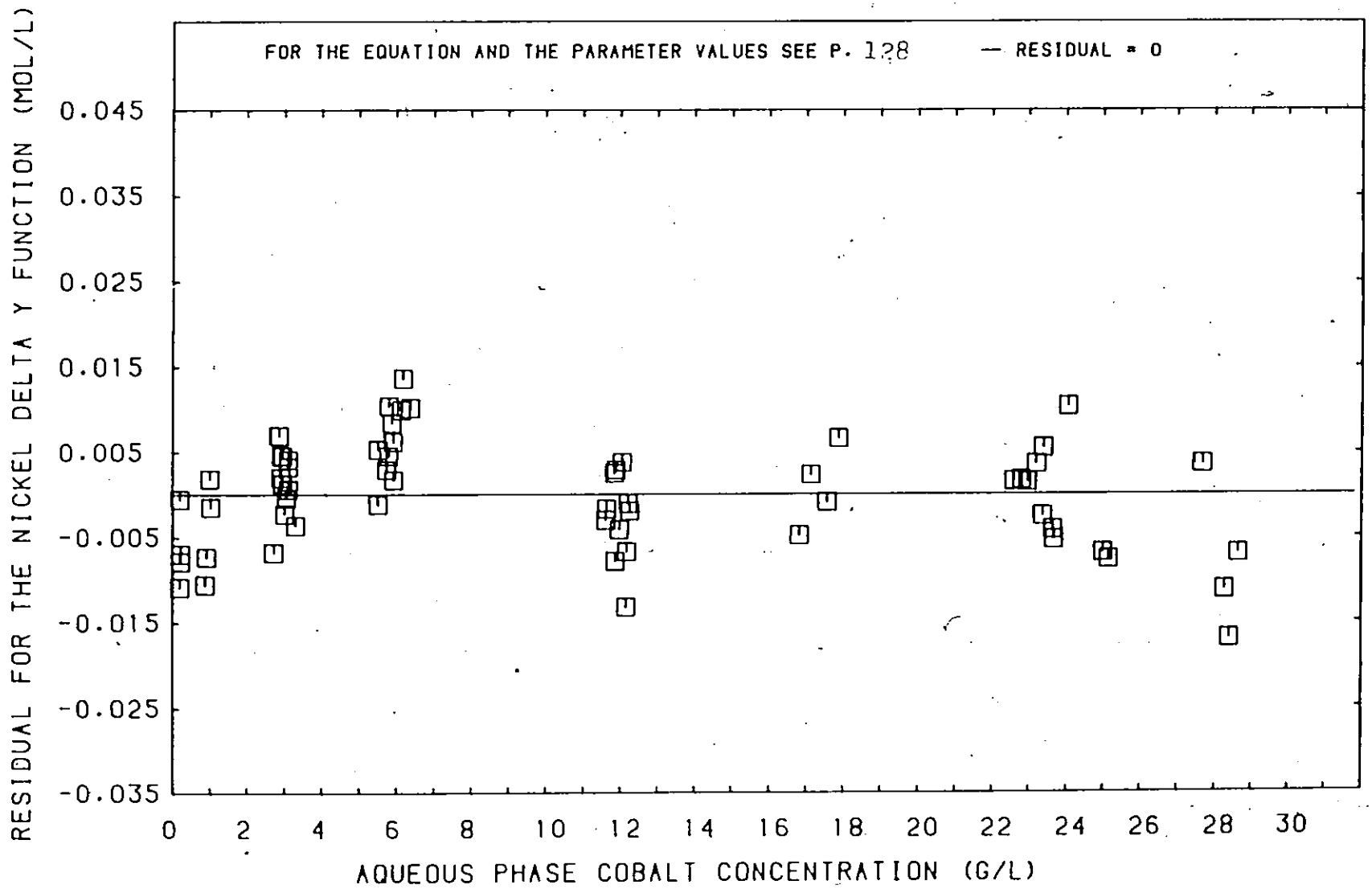


FIGURE 10C. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE COBALT CONC. FOR THE NICKEL DELTA Y FUNCTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

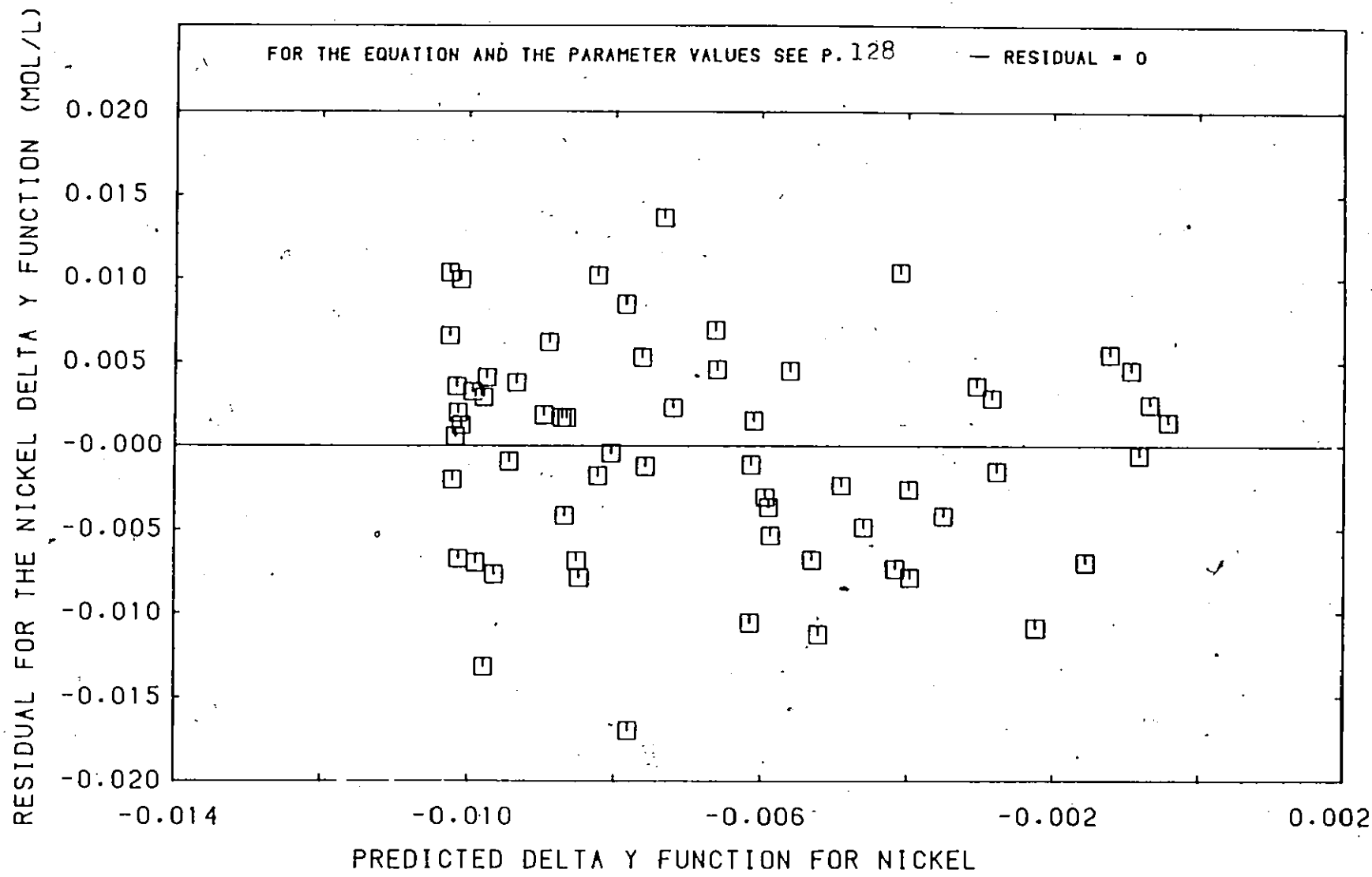


FIGURE 10D. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED NICKEL DELTA Y FUNCTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

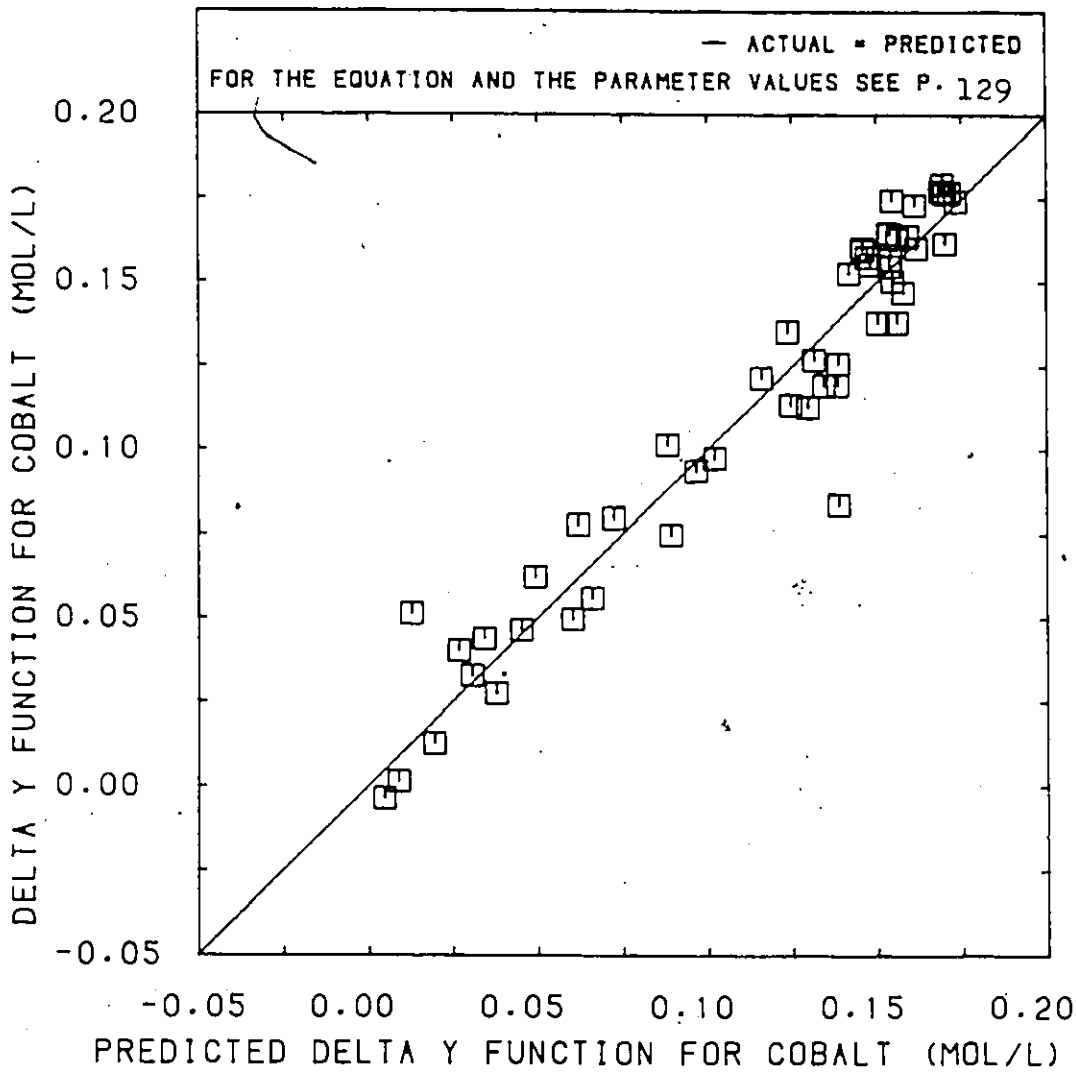


FIGURE 11A. COMPARISON BETWEEN THE ACTUAL AND PREDICTED DELTA Y FUNCTIONS FOR COBALT AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.5-6.4; A/O = 1.

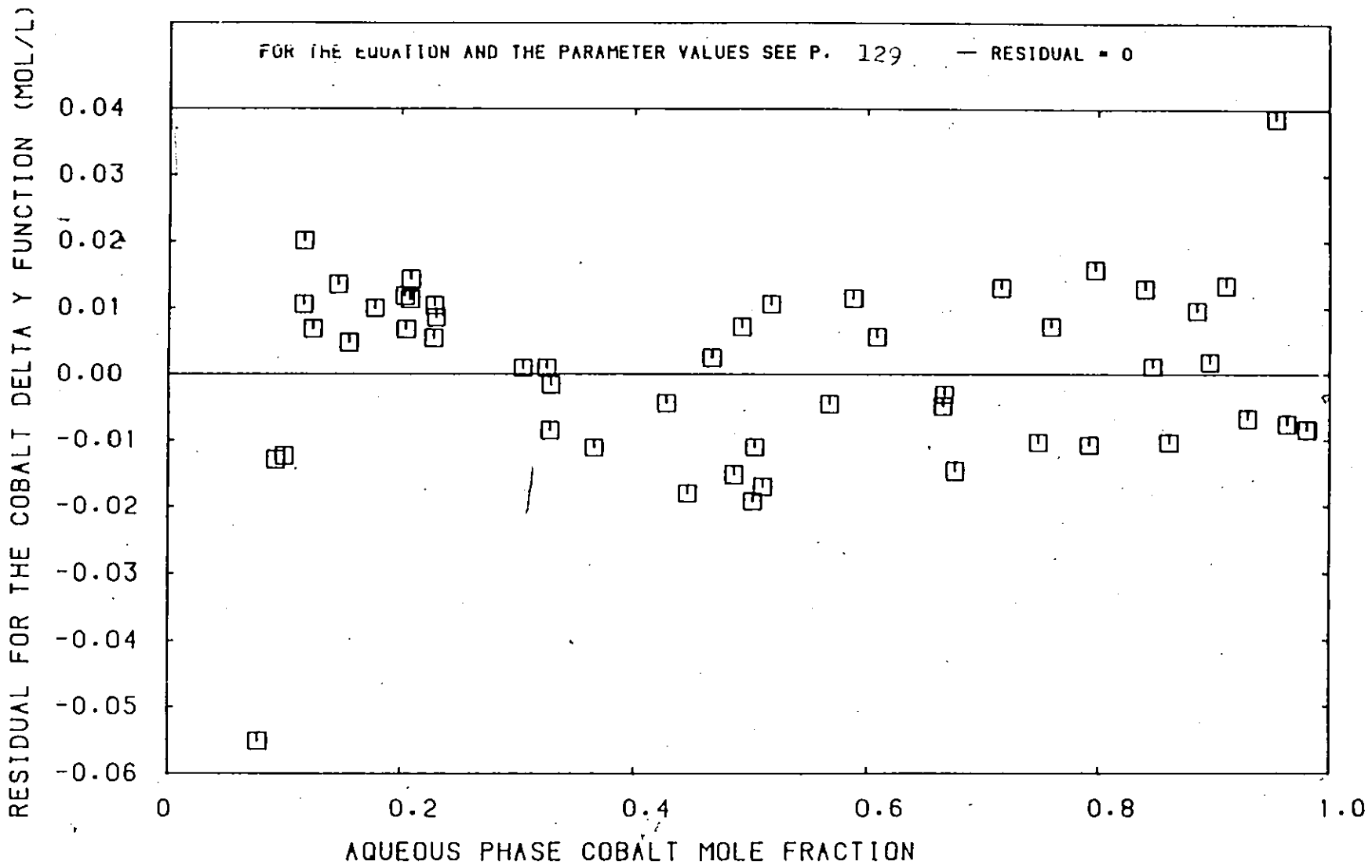


FIGURE 11B. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE COBALT MOLE FRACTION FOR THE COBALT DELTA Y FUNCTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

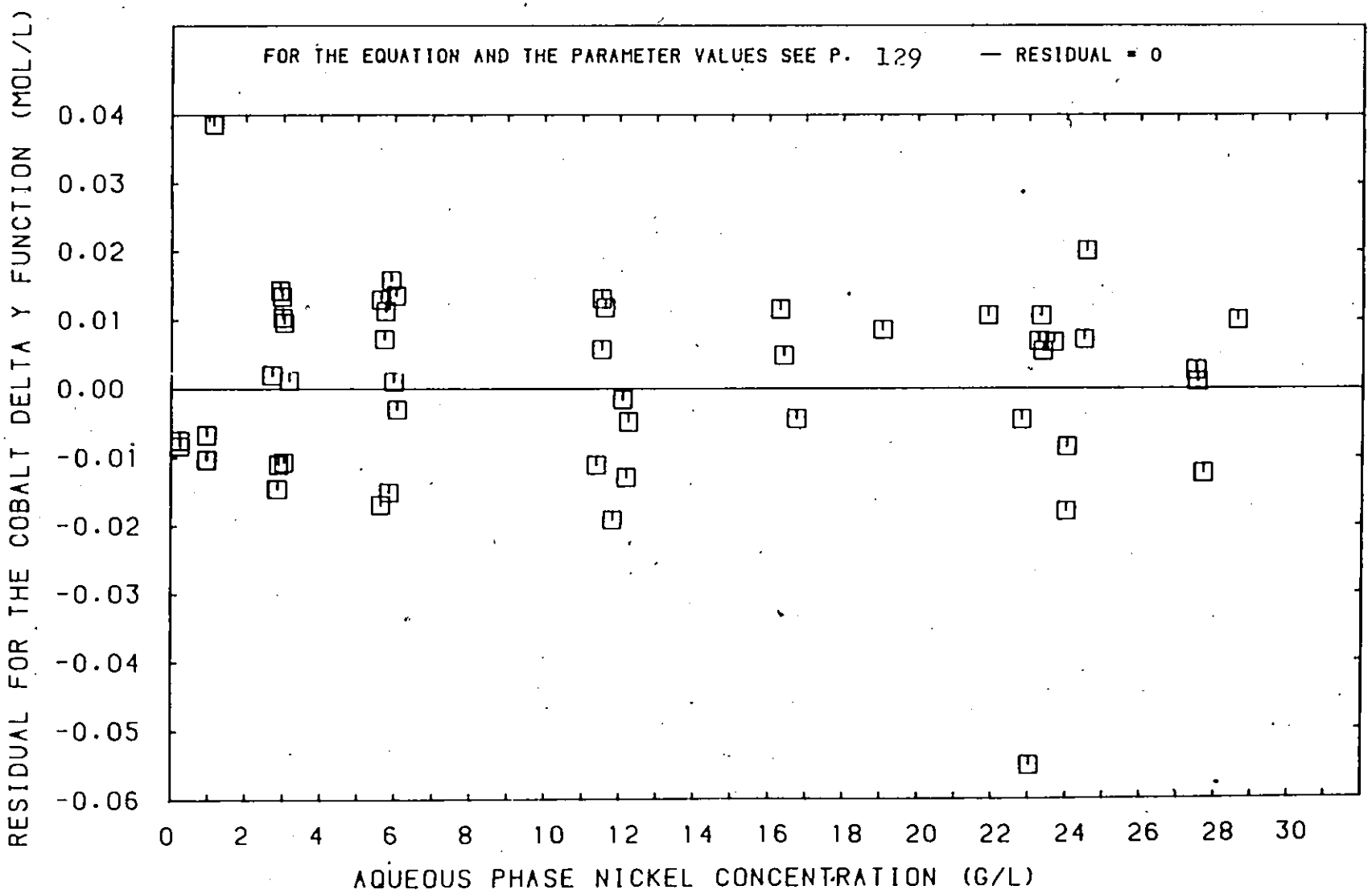


FIGURE 11C. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE NICKEL CONC. FOR THE COBALT DELTA Y FUNCTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

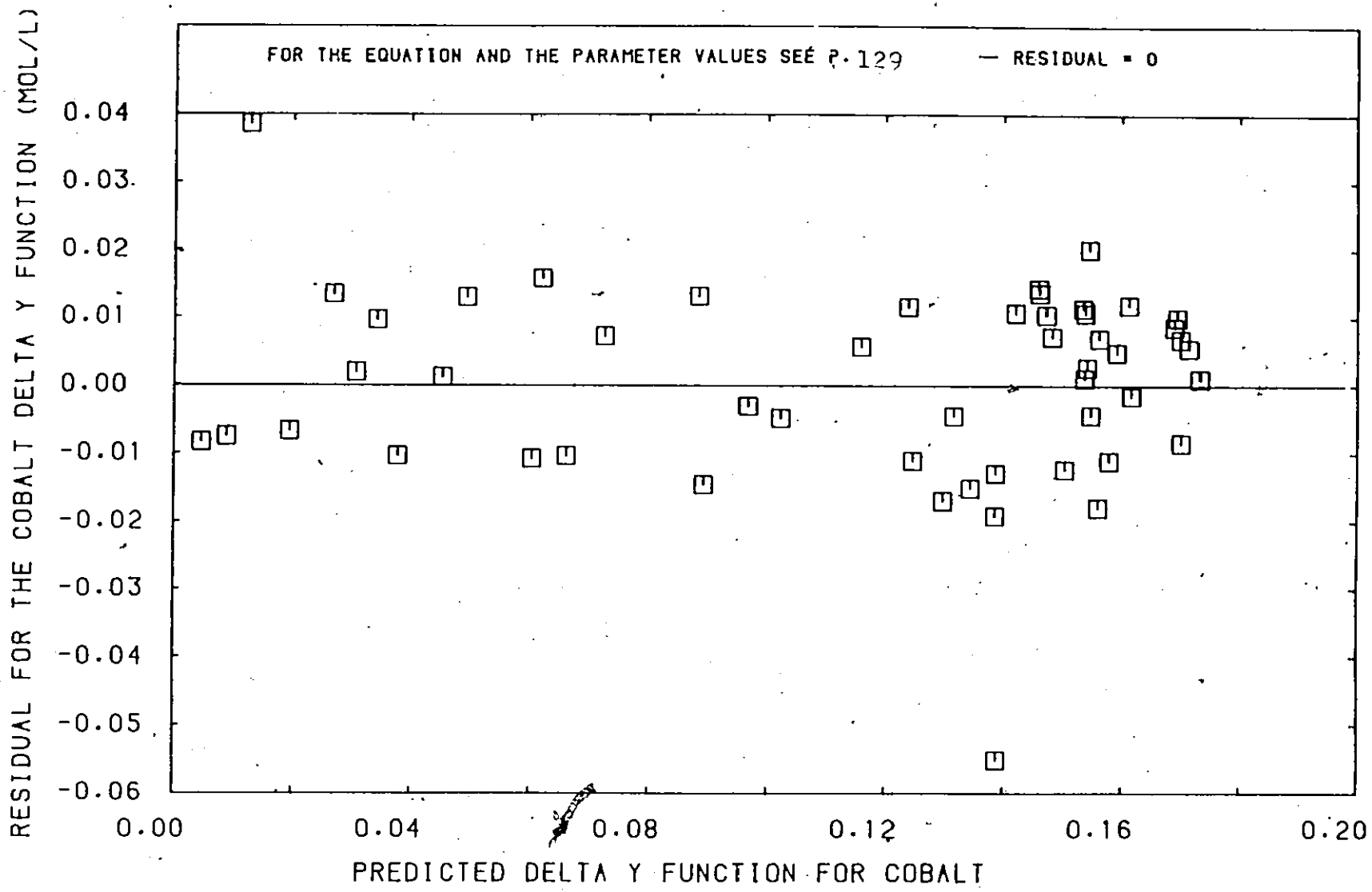


FIGURE 11D. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED COBALT DELTA Y FUNCTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

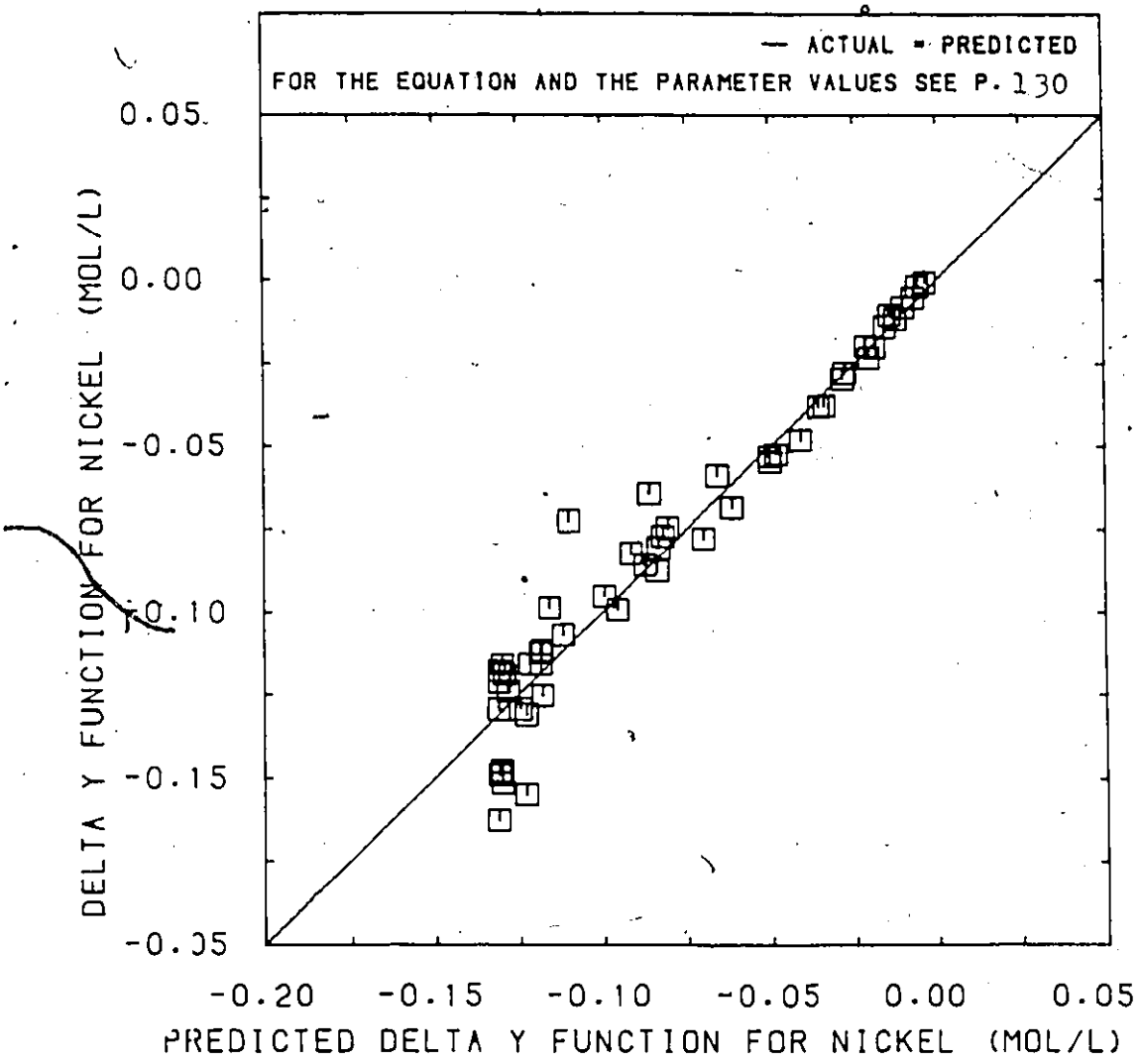


FIGURE 12A. COMPARISON BETWEEN THE ACTUAL AND PREDICTED DELTA Y FUNCTIONS FOR NICKEL AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.5-6.3; A/O = 1.

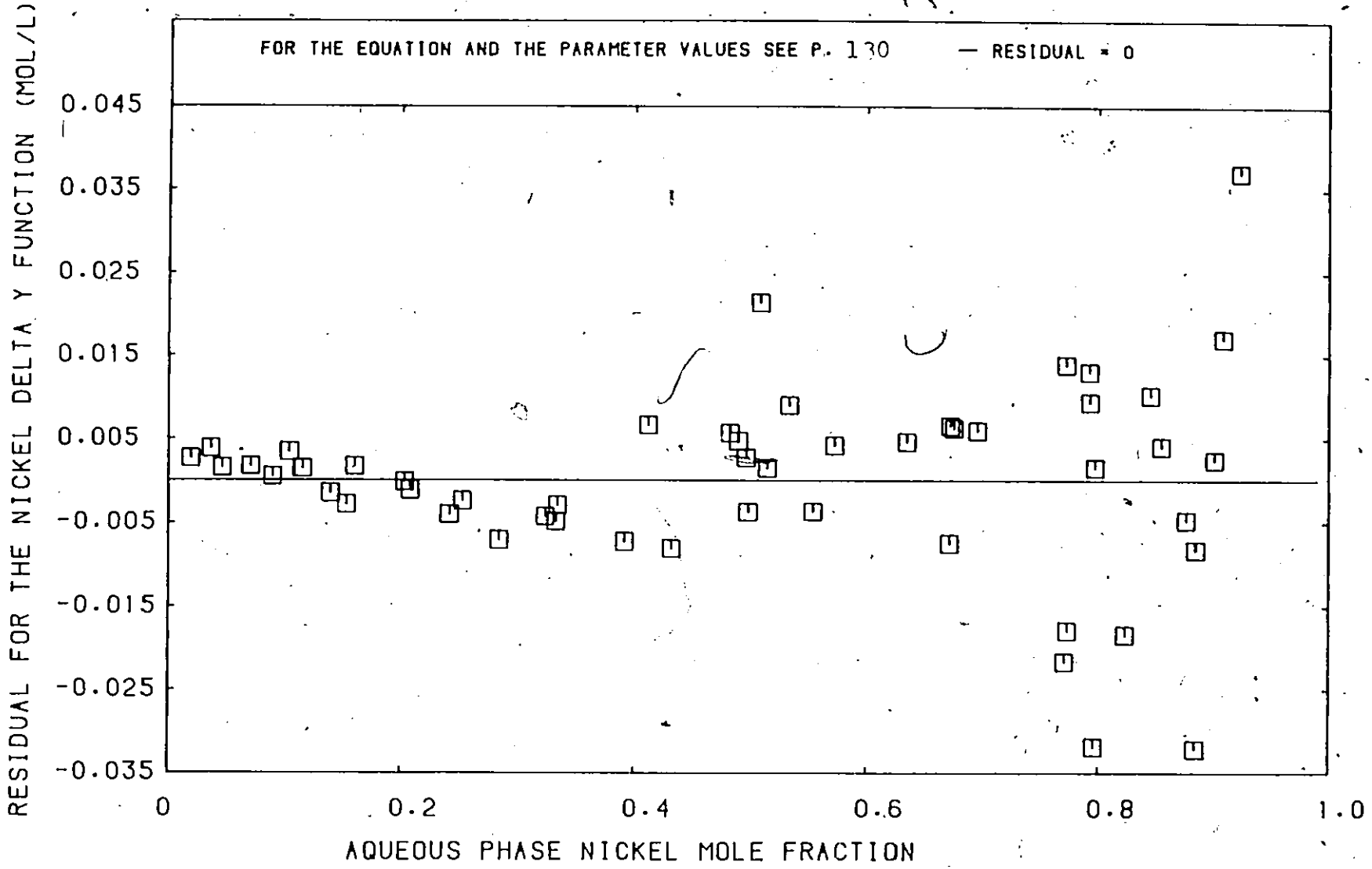


FIGURE 128. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE NICKEL MOLE FRACTION FOR THE NICKEL DELTA Y FUNCTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

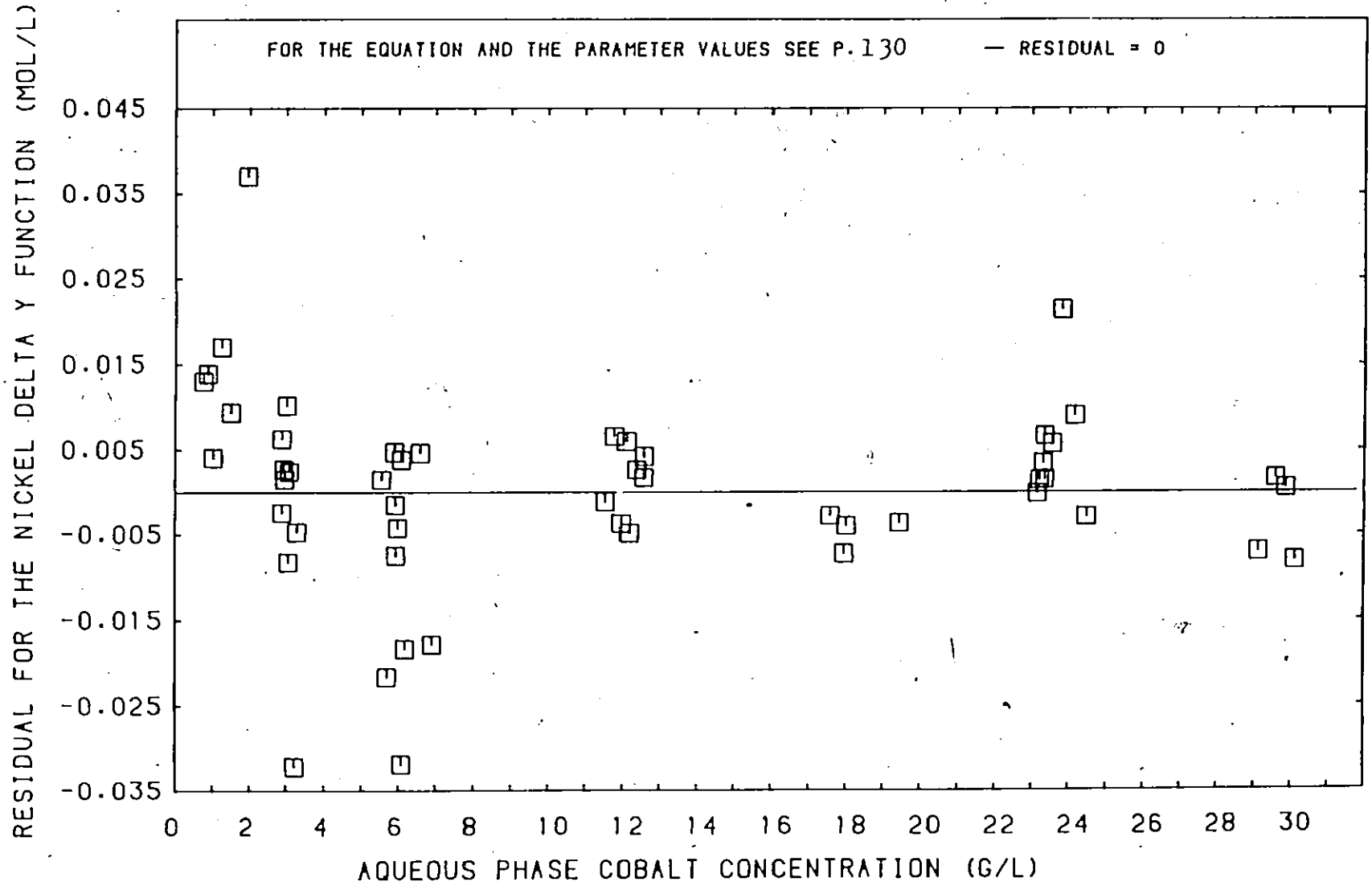


FIGURE 12C. RESIDUAL PLOT AS A FUNCTION OF AQ. PHASE COBALT CONC. FOR THE NICKEL DELTA Y FUNCTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

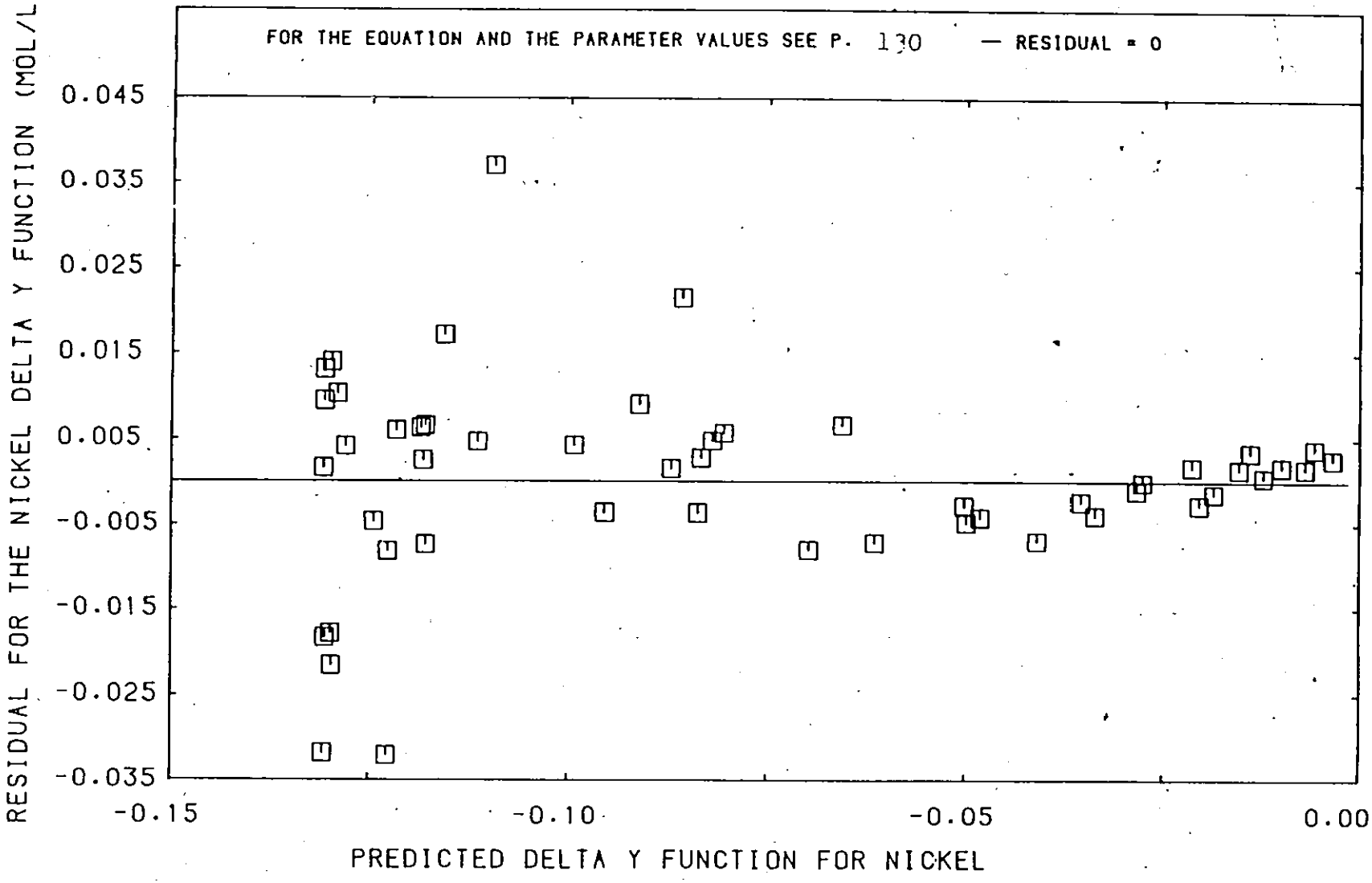


FIGURE 12D. RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED NICKEL DELTA Y FUNCTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

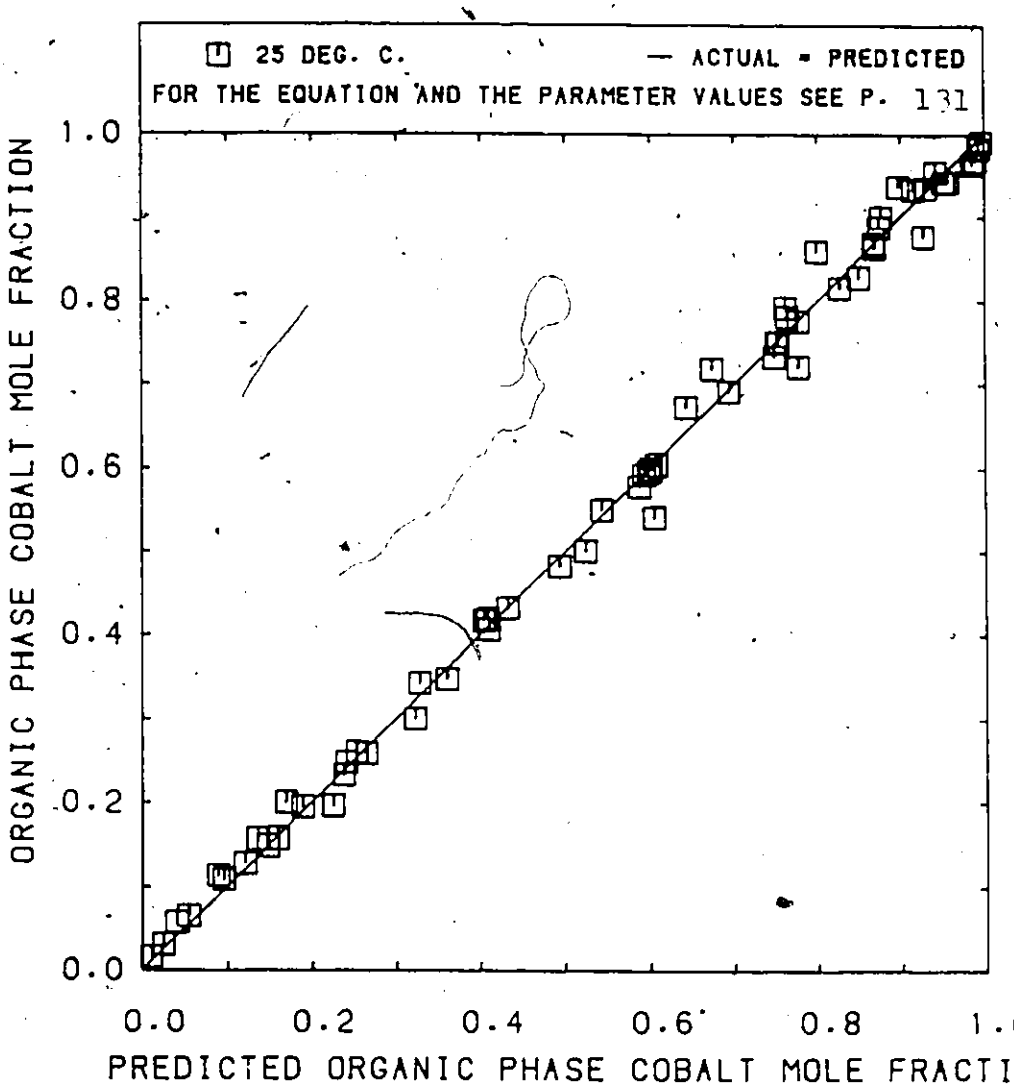


FIGURE 13A1. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE COBALT MOLE FRACTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.4; A/O = 1.

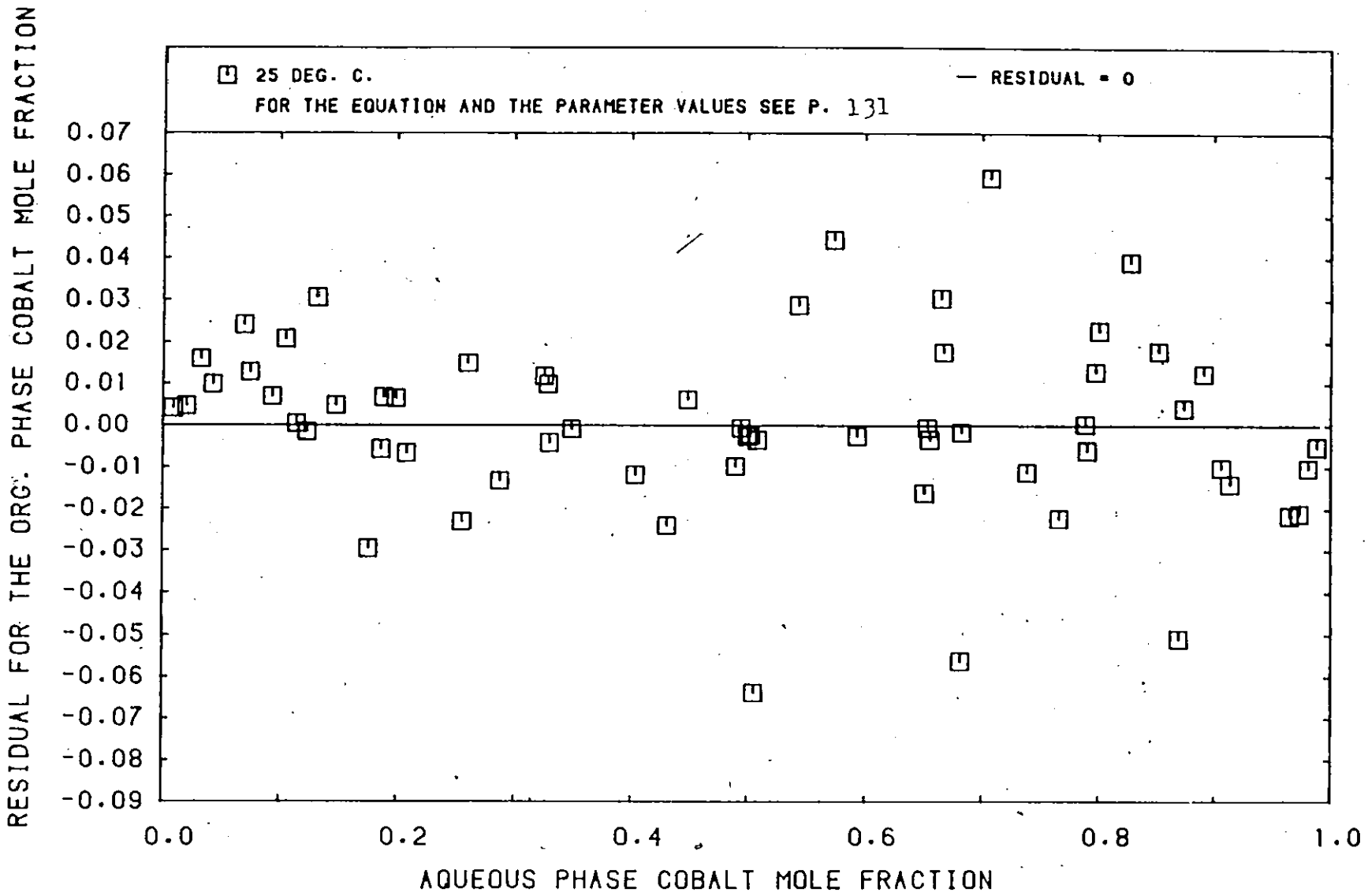


FIGURE 131 RESIDUAL PLOT AS A FUNCTION OF AQUEOUS PHASE COBALT MOLE FRACTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

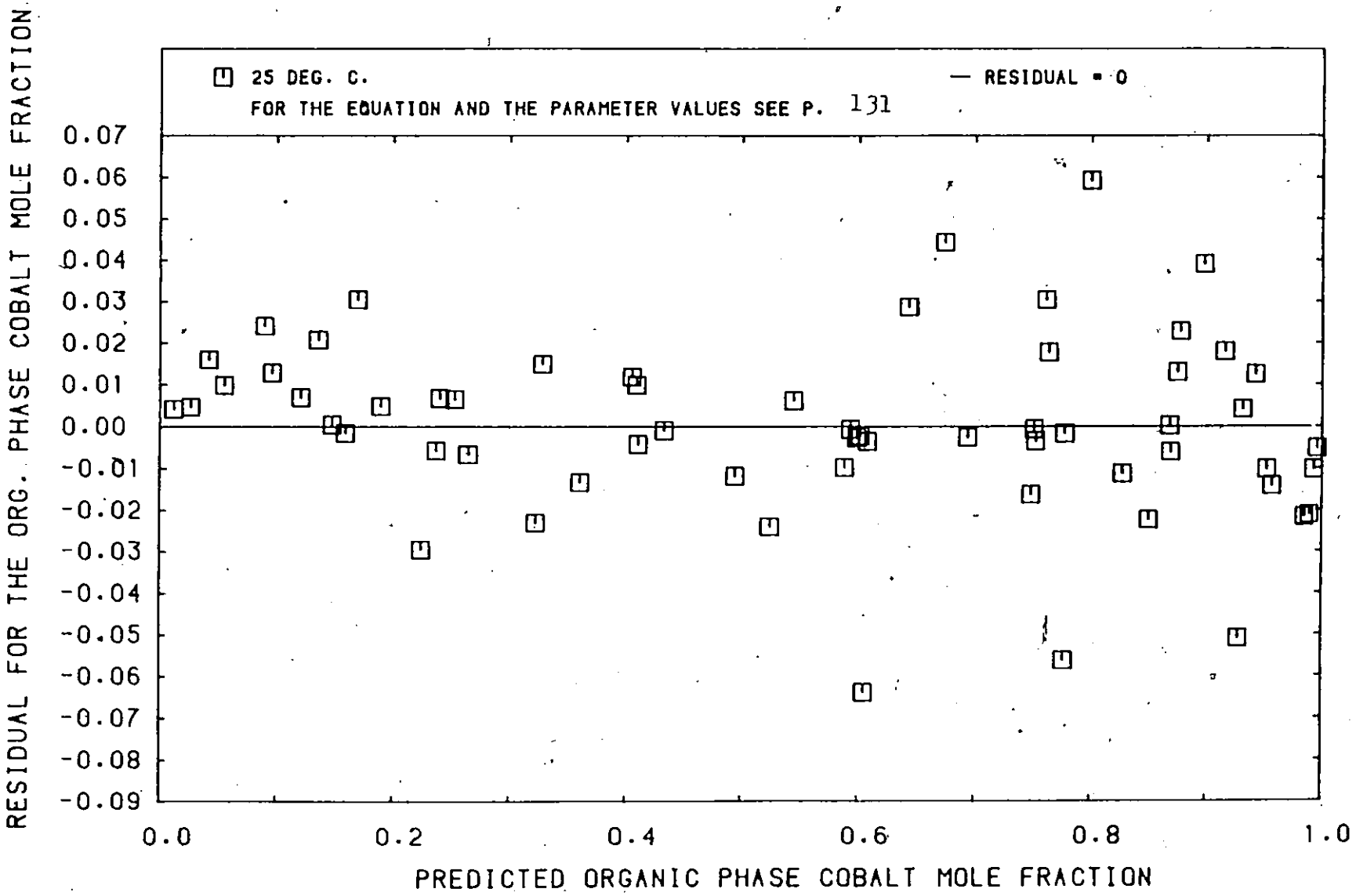


FIGURE 13C1 RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED ORGANIC PHASE COBALT MOLE FRACTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

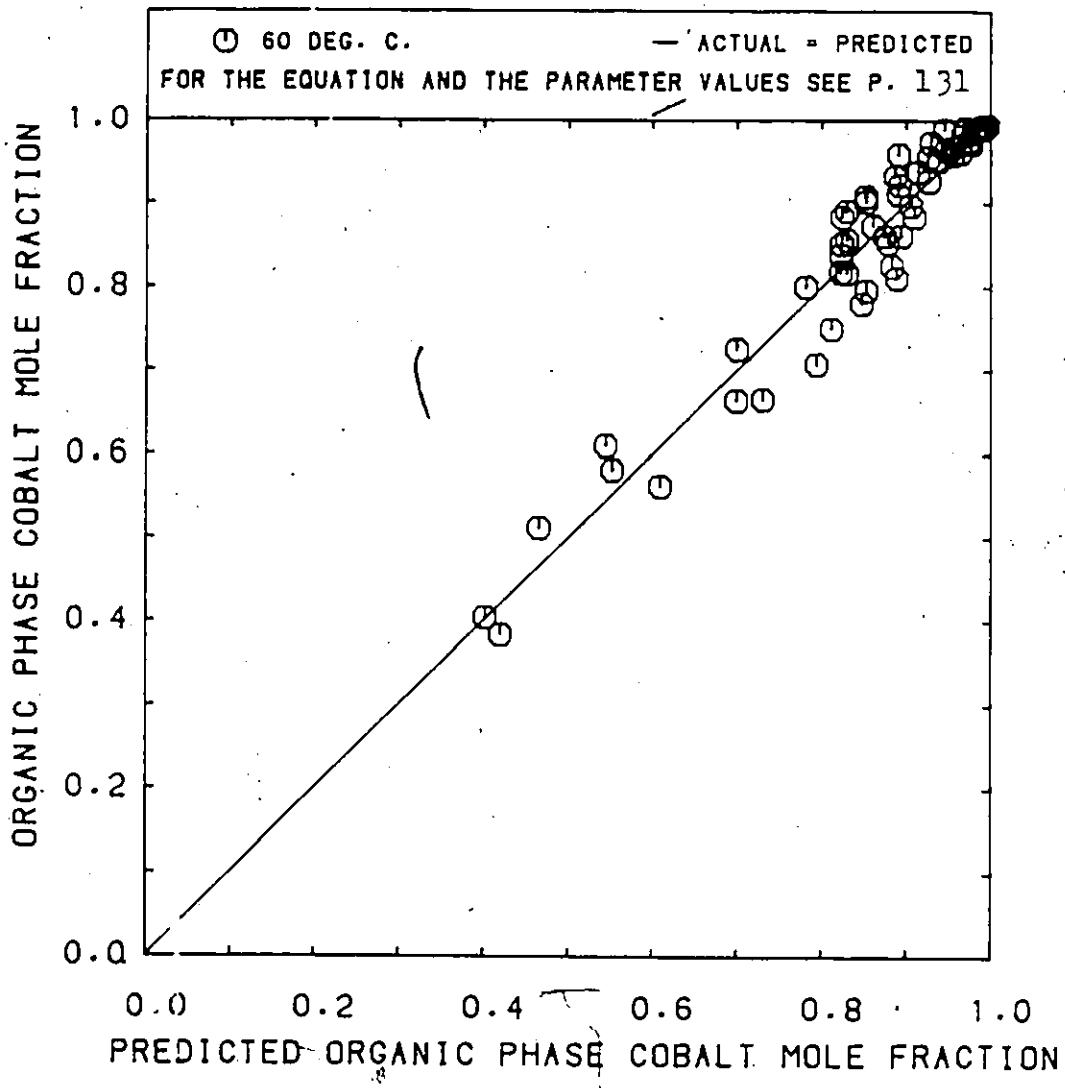


FIGURE 13A2. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE COBALT MOLE FRACTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH = 5.5-6.4; A/O = 1.

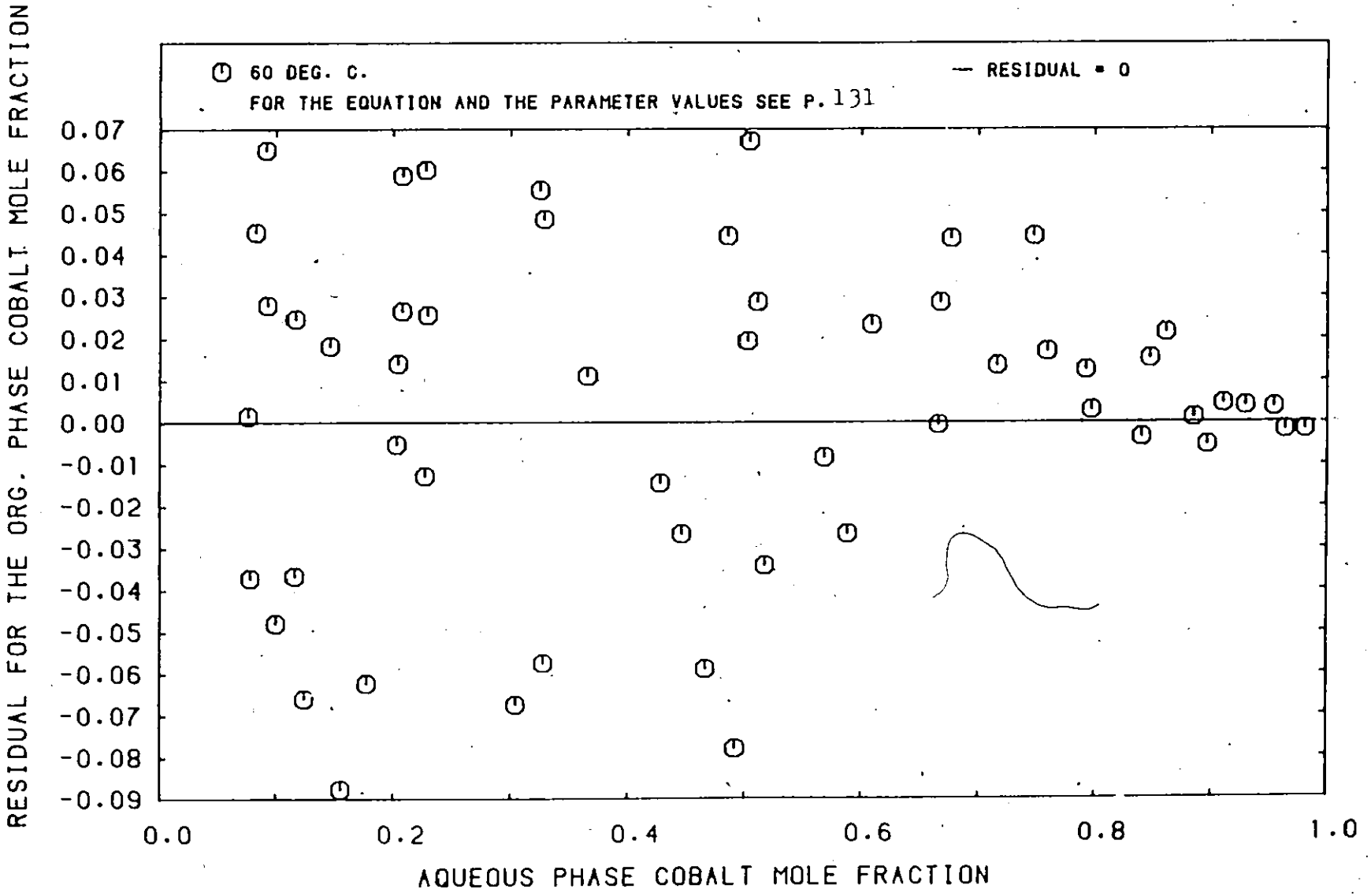


FIGURE 1332 RESIDUAL PLOT AS A FUNCTION OF AQUEOUS PHASE COBALT MOLE FRACTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

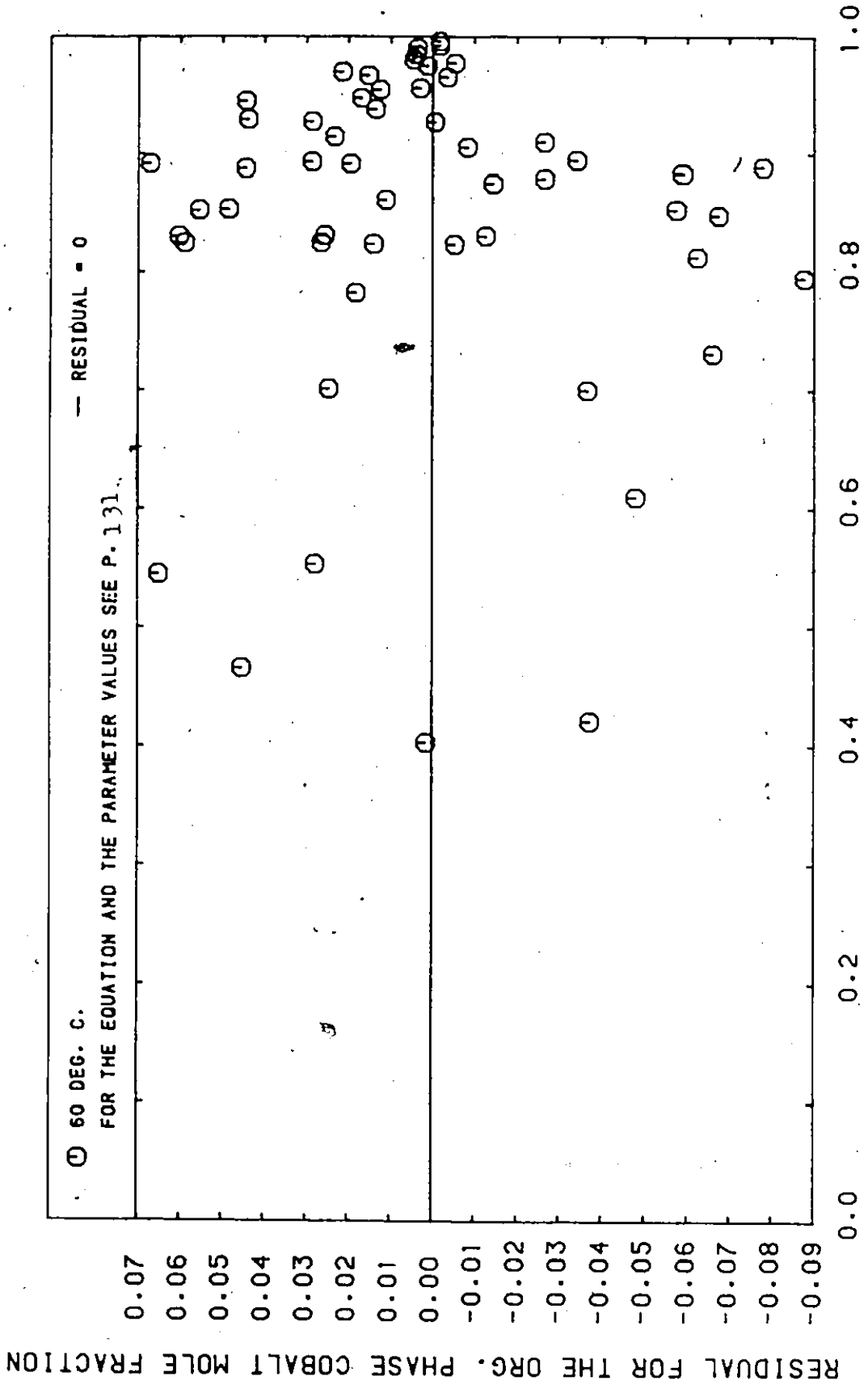


FIGURE 13C2 RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED ORGANIC PHASE COBALT MOLE FRACTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL (OX3641), 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

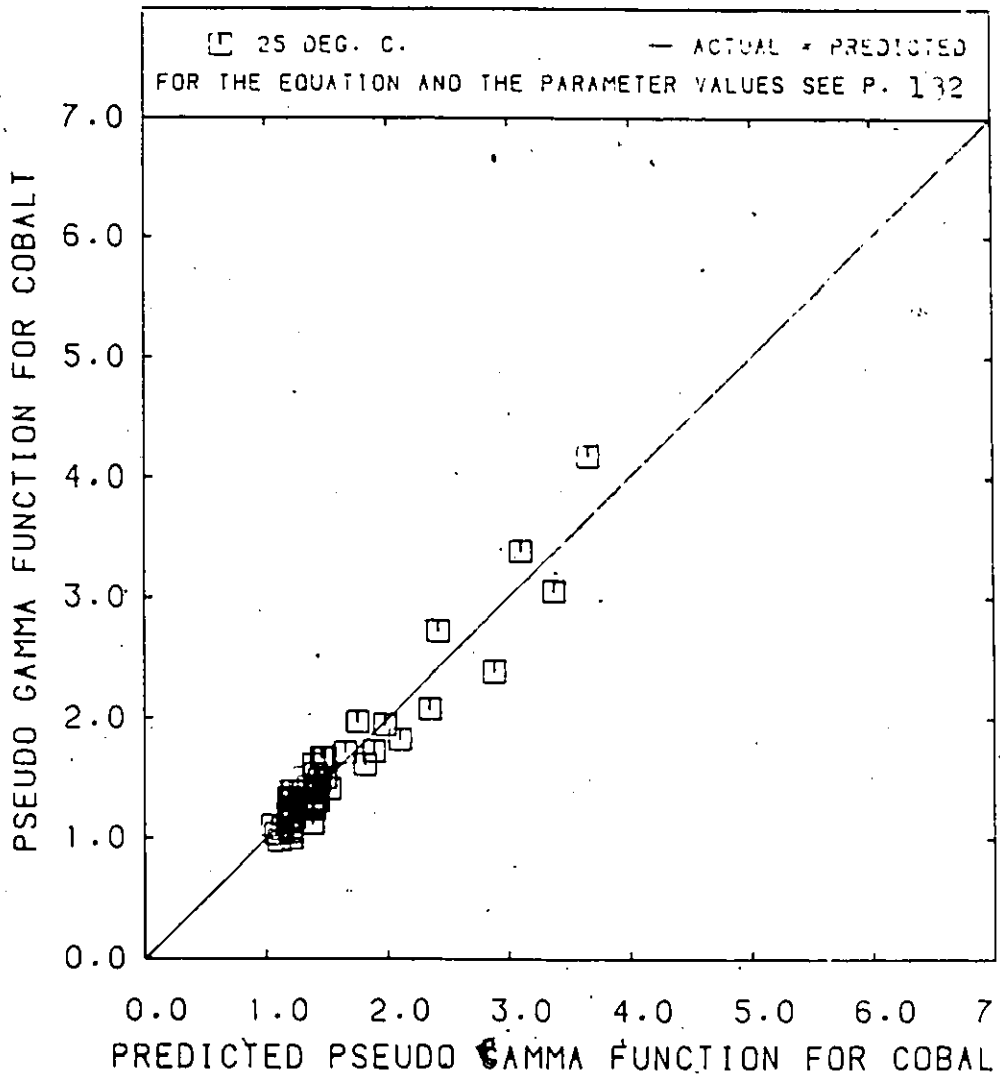


FIGURE 14a1. COMPARISON BETWEEN THE ACTUAL AND PREDICTED PSEUDO GAMMA FUNCTIONS FOR COBALT AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.4; A/O = 1.

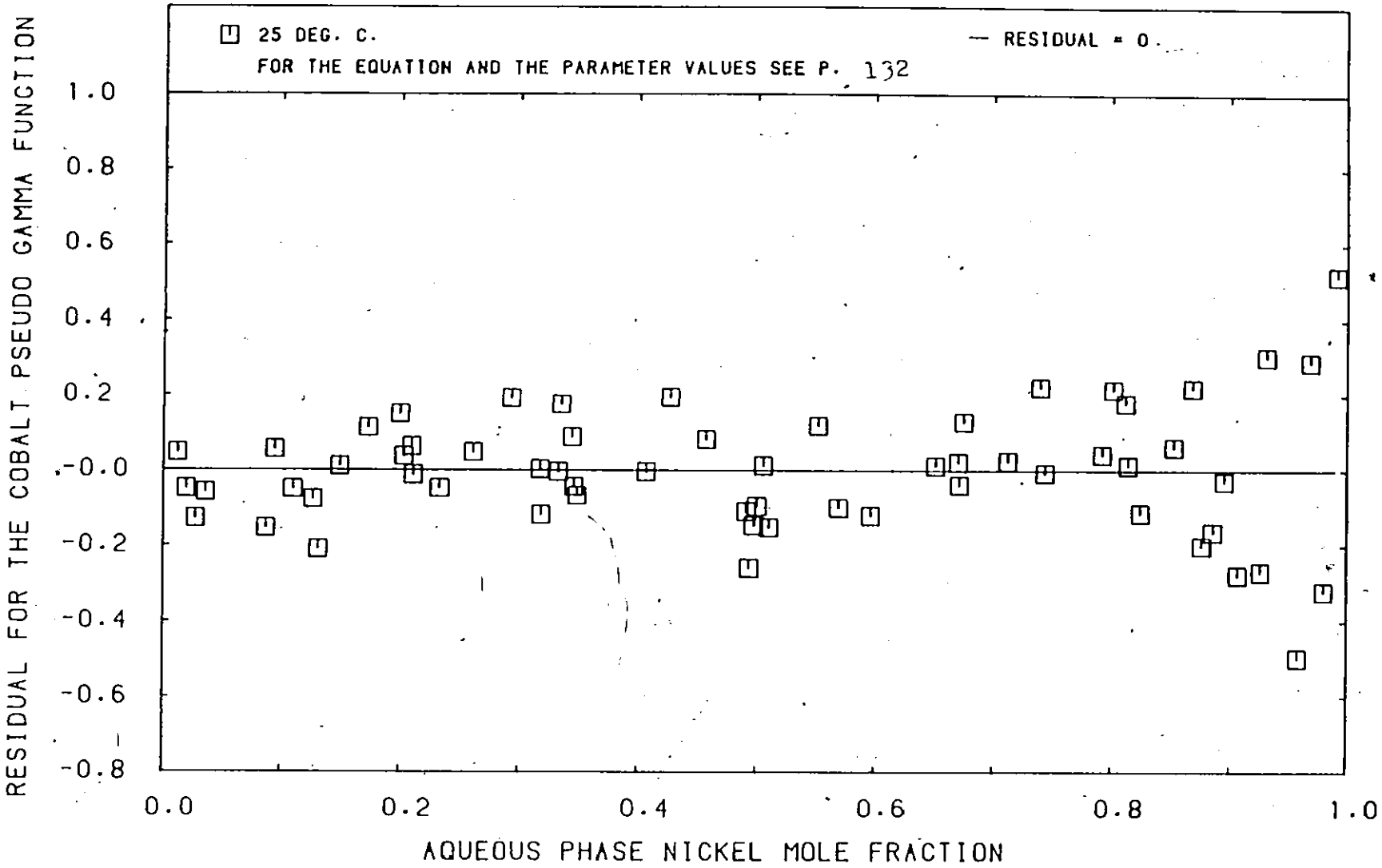


FIGURE 14B1 RESIDUAL PLOT AS A FUNCTION OF AQUEOUS PHASE NICKEL MOLE FRACTION FOR THE PSEUDO GAMMA COBALT FUNCTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

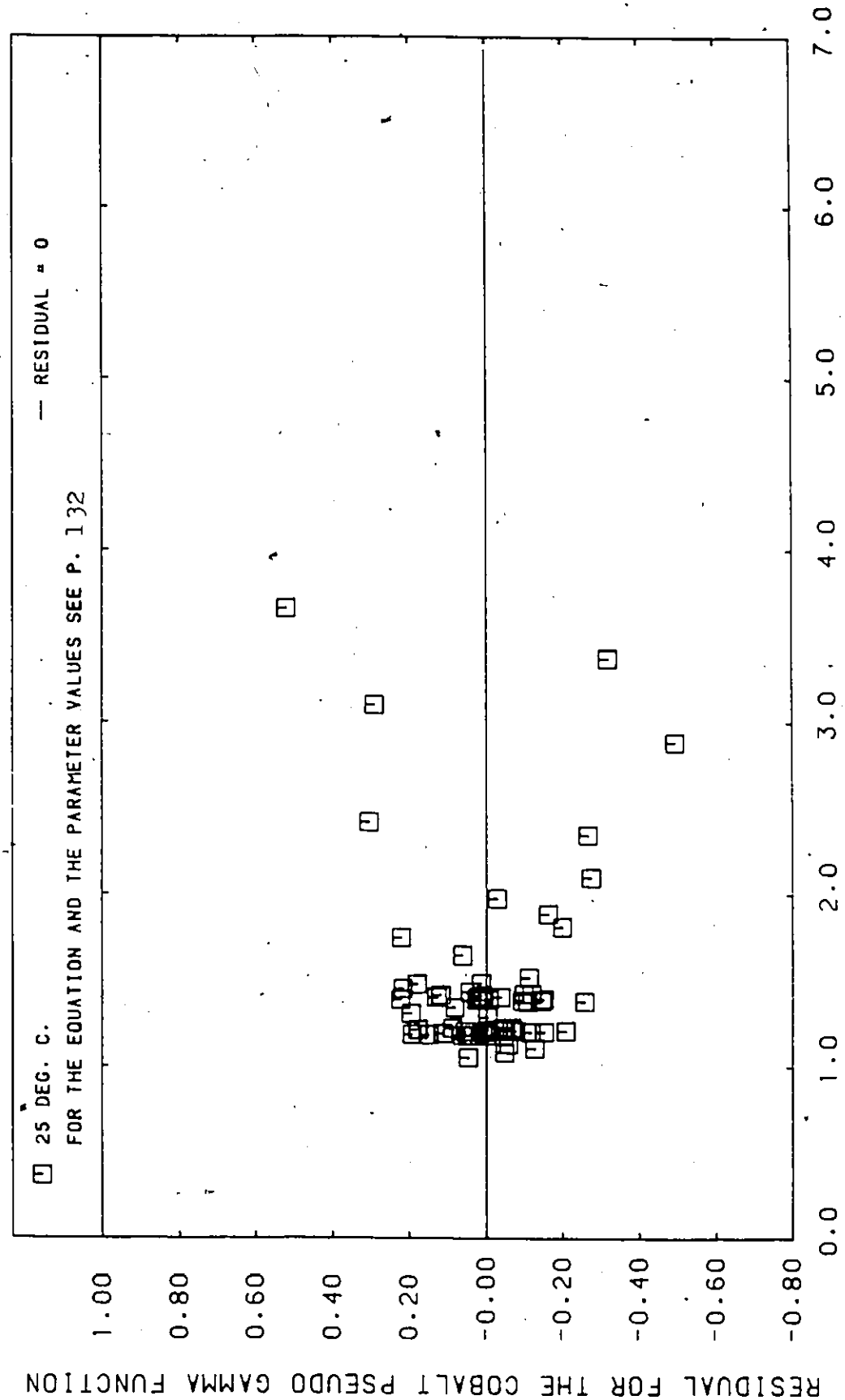


FIGURE 140: RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED COBALT PSEUDO GAMMA FUNCTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP, A/O = 1.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

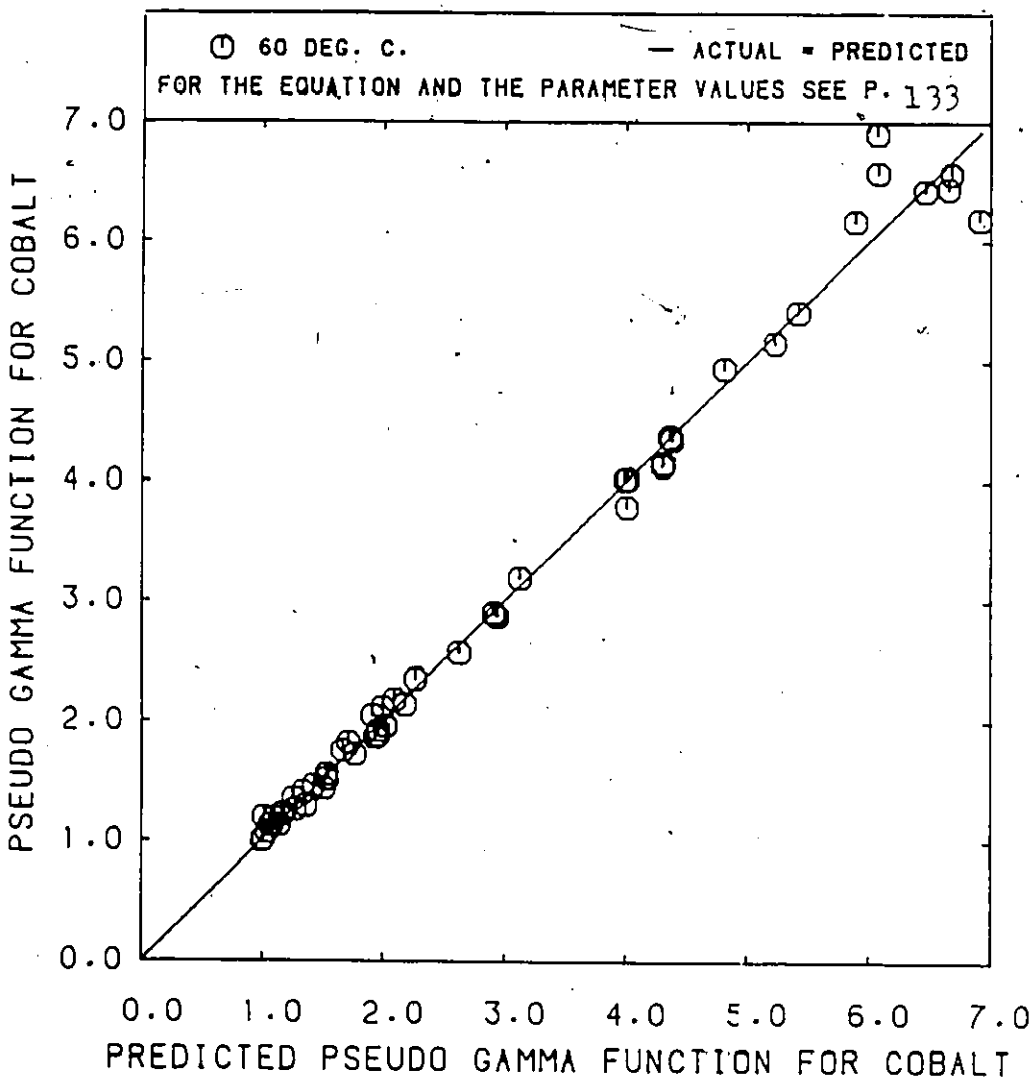


FIGURE 14A2. COMPARISON BETWEEN THE ACTUAL AND PREDICTED PSEUDO GAMMA FUNCTIONS FOR COBALT AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4,
EQUILIBRIUM PH = 5.5-6.4; A/O = 1.

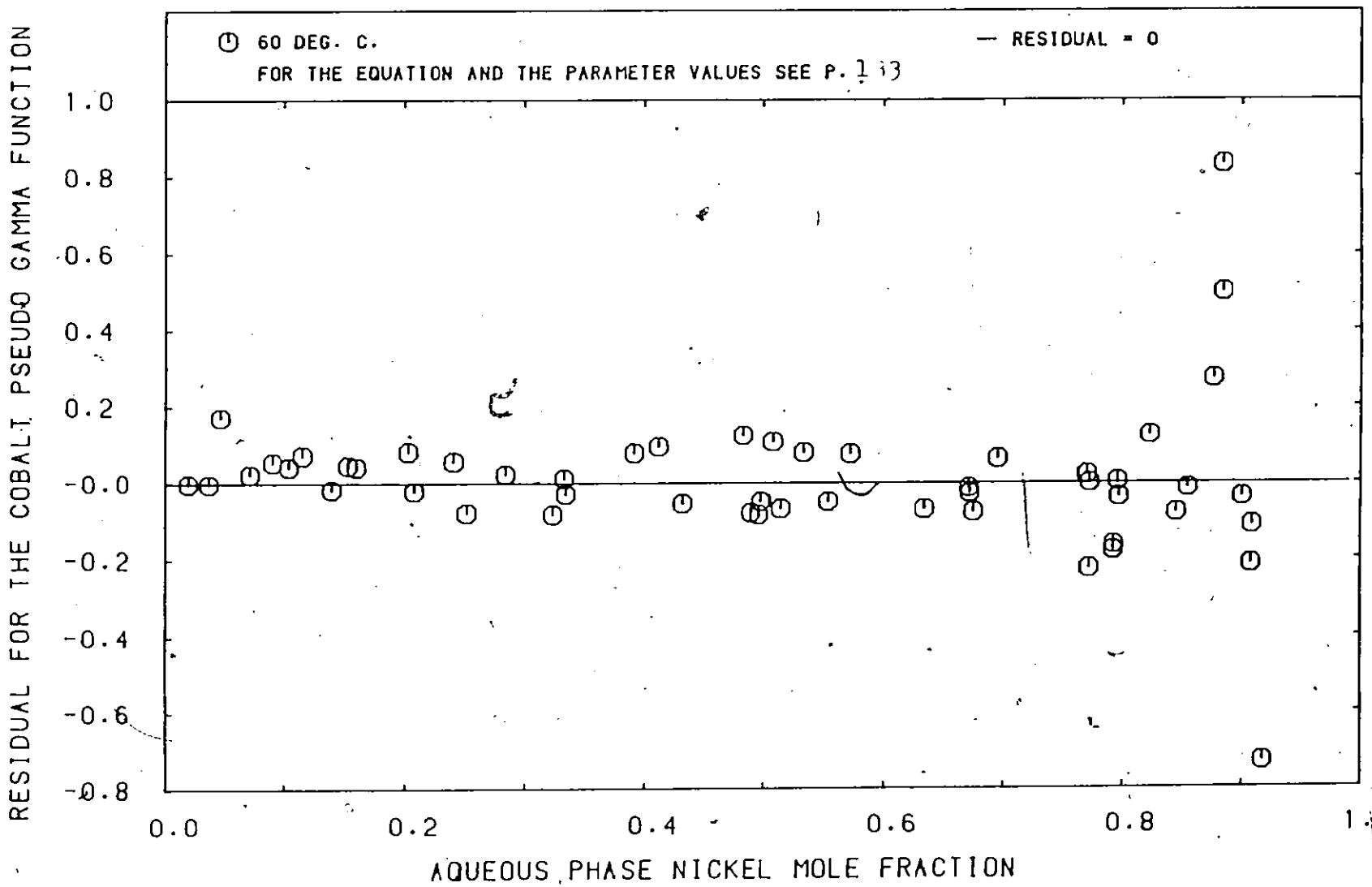


FIGURE 1432 RESIDUAL PLOT AS A FUNCTION OF AQUEOUS PHASE NICKEL MOLE FRACTION FOR THE PSEUDO GAMMA COBALT FUNCTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

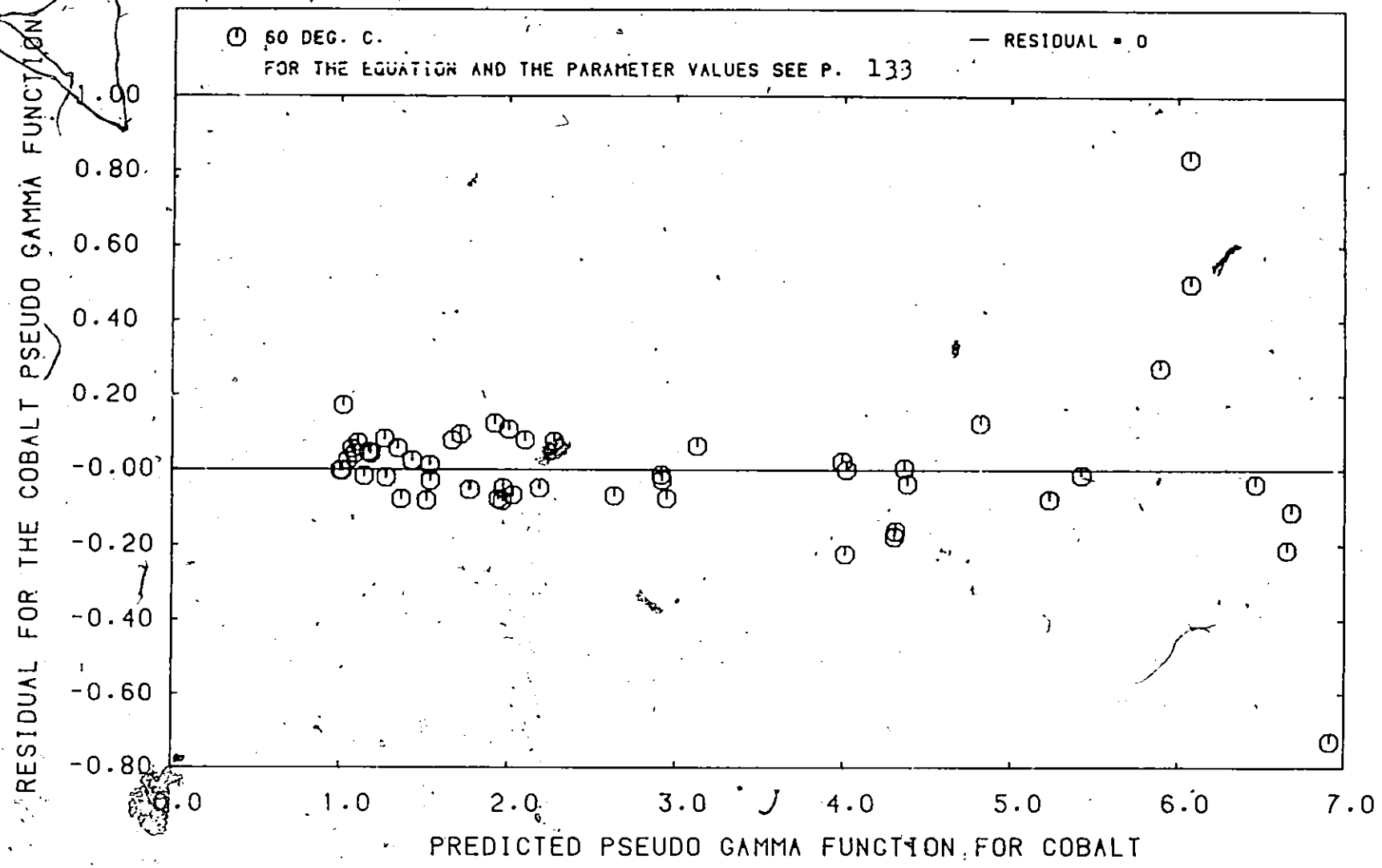


FIGURE 14C2 RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED COBALT PSEUDO GAMMA FUNCTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

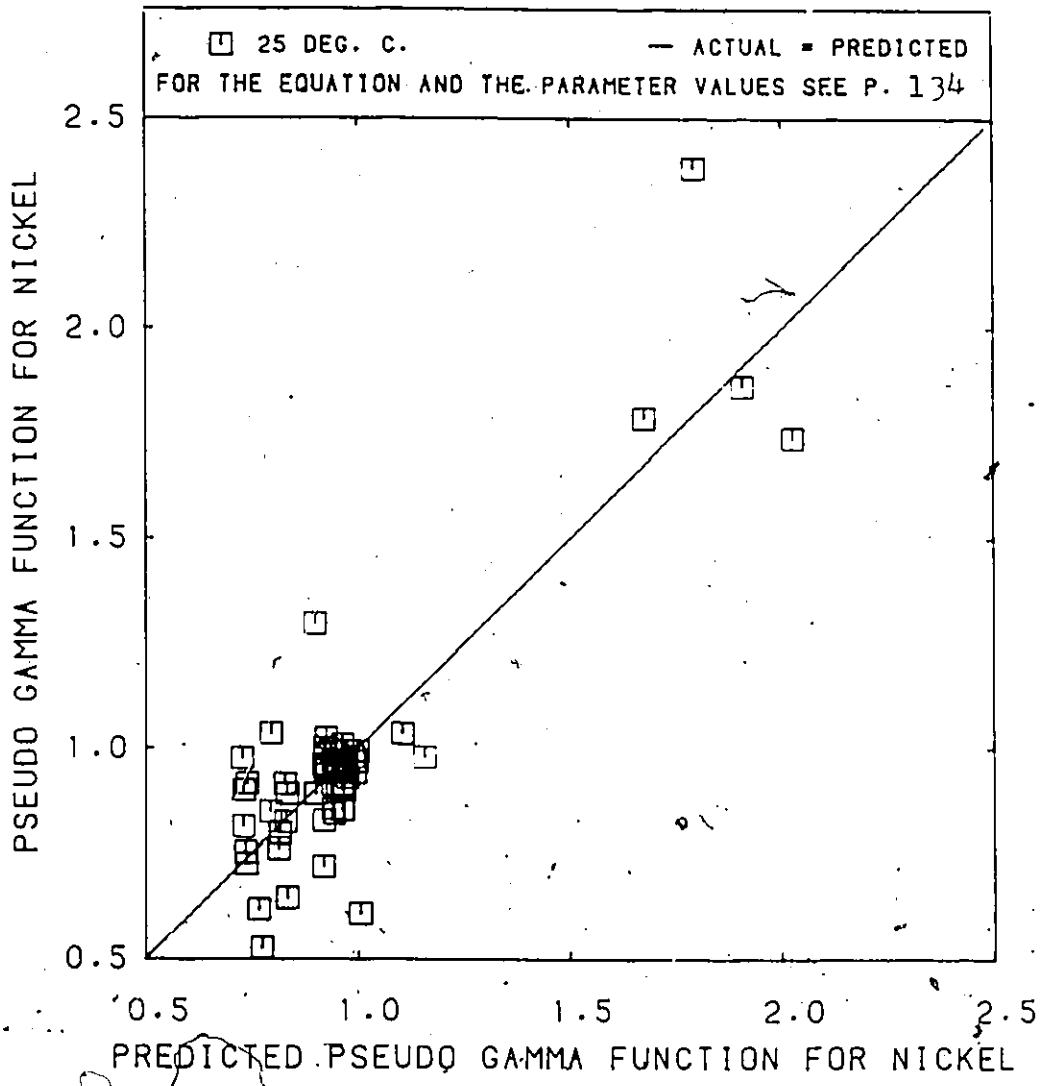


FIGURE 15A1. COMPARISON BETWEEN THE ACTUAL AND PREDICTED PSEUDO GAMMA FUNCTIONS FOR NICKEL AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.4; A/O = 1.

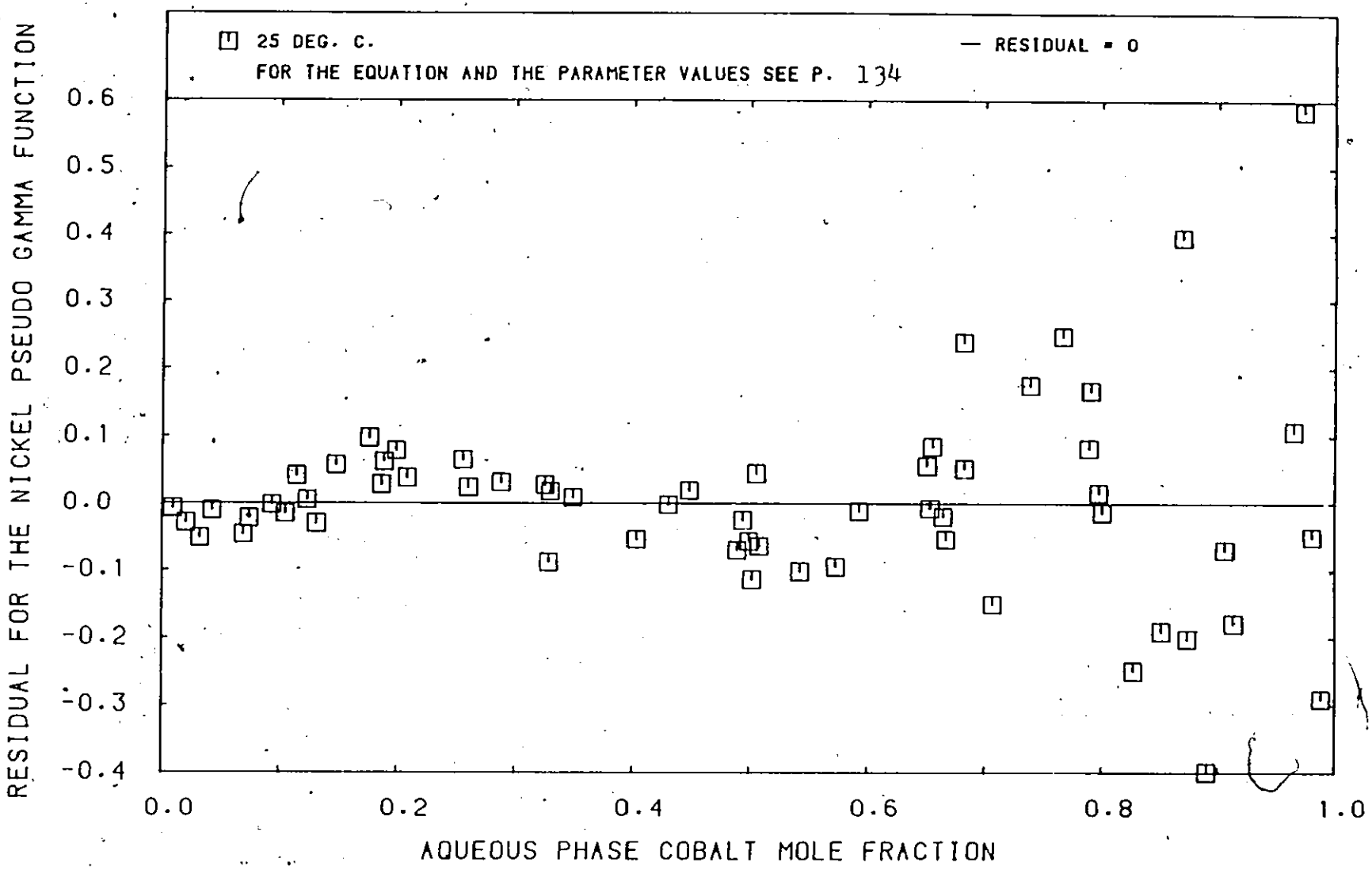


FIGURE15B1,RESIDUAL PLOT AS A FUNCTION OF AQUEOUS PHASE COBALT MOLE FRACTION FOR THE PSEUDO GAMMA NICKEL FUNCTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

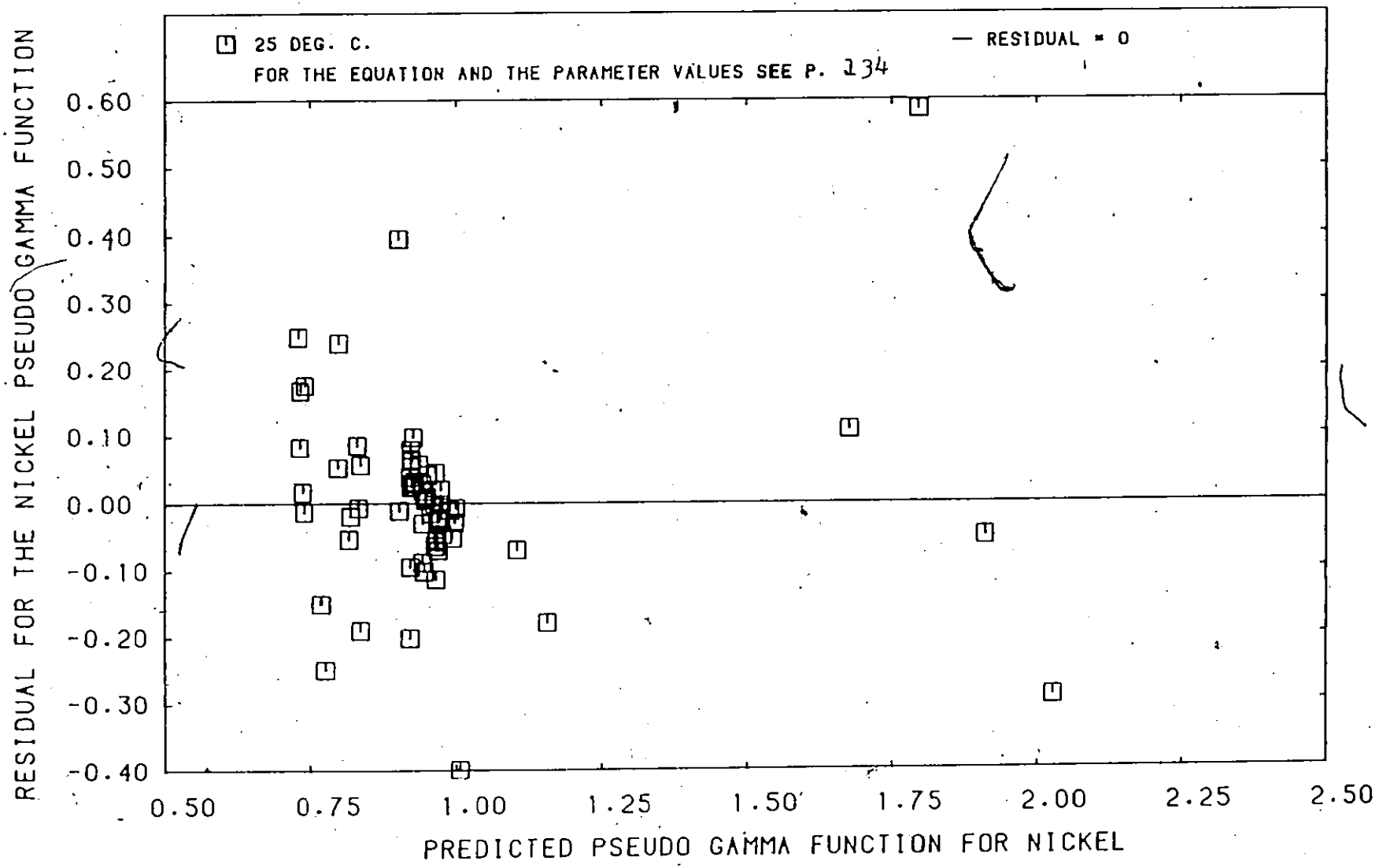


FIGURE 15C1 RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED NICKEL PSEUDO GAMMA FUNCTION AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

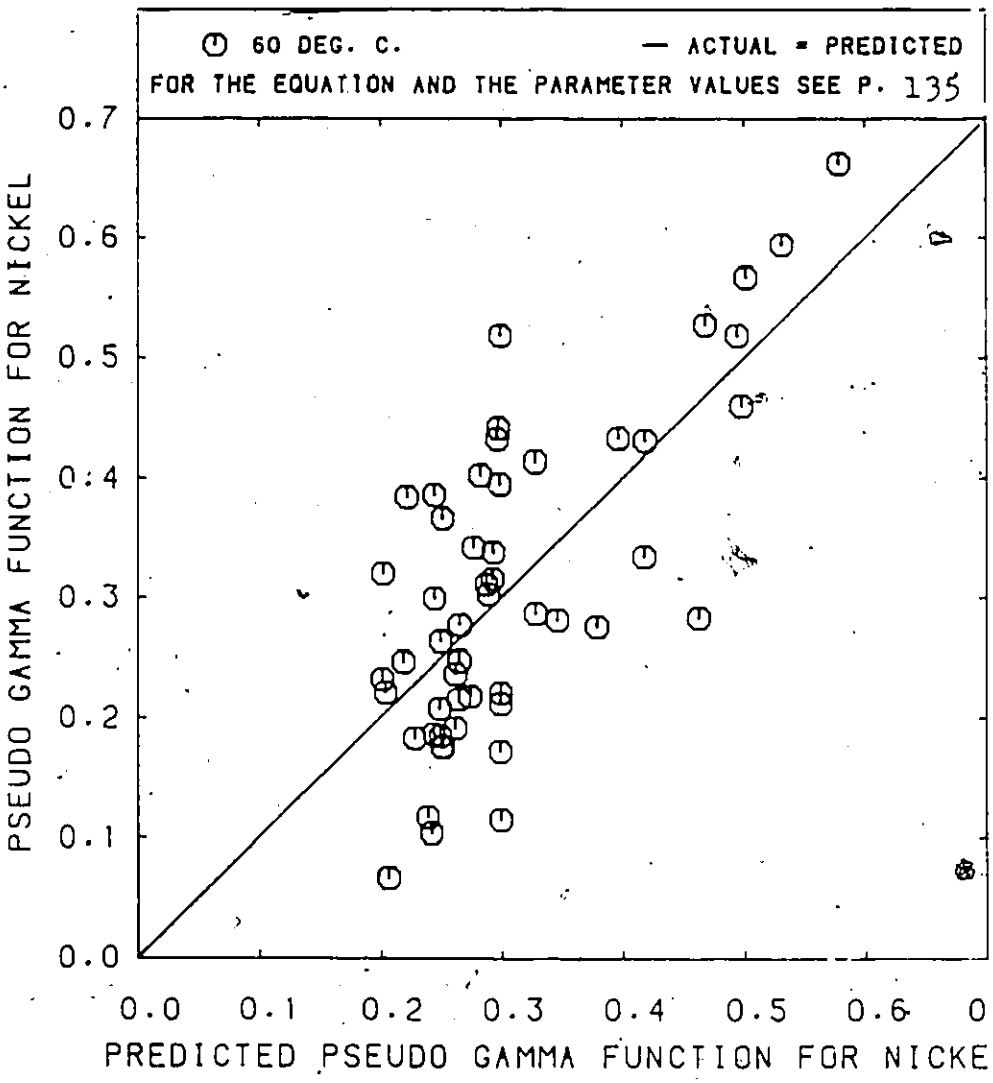


FIGURE 15A2. COMPARISON BETWEEN THE ACTUAL AND PREDICTED PSEUDO GAMMA FUNCTIONS FOR NICKEL AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DXJ641. 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4.
EQUILIBRIUM PH = 5.5-6.4; A/O = 1.

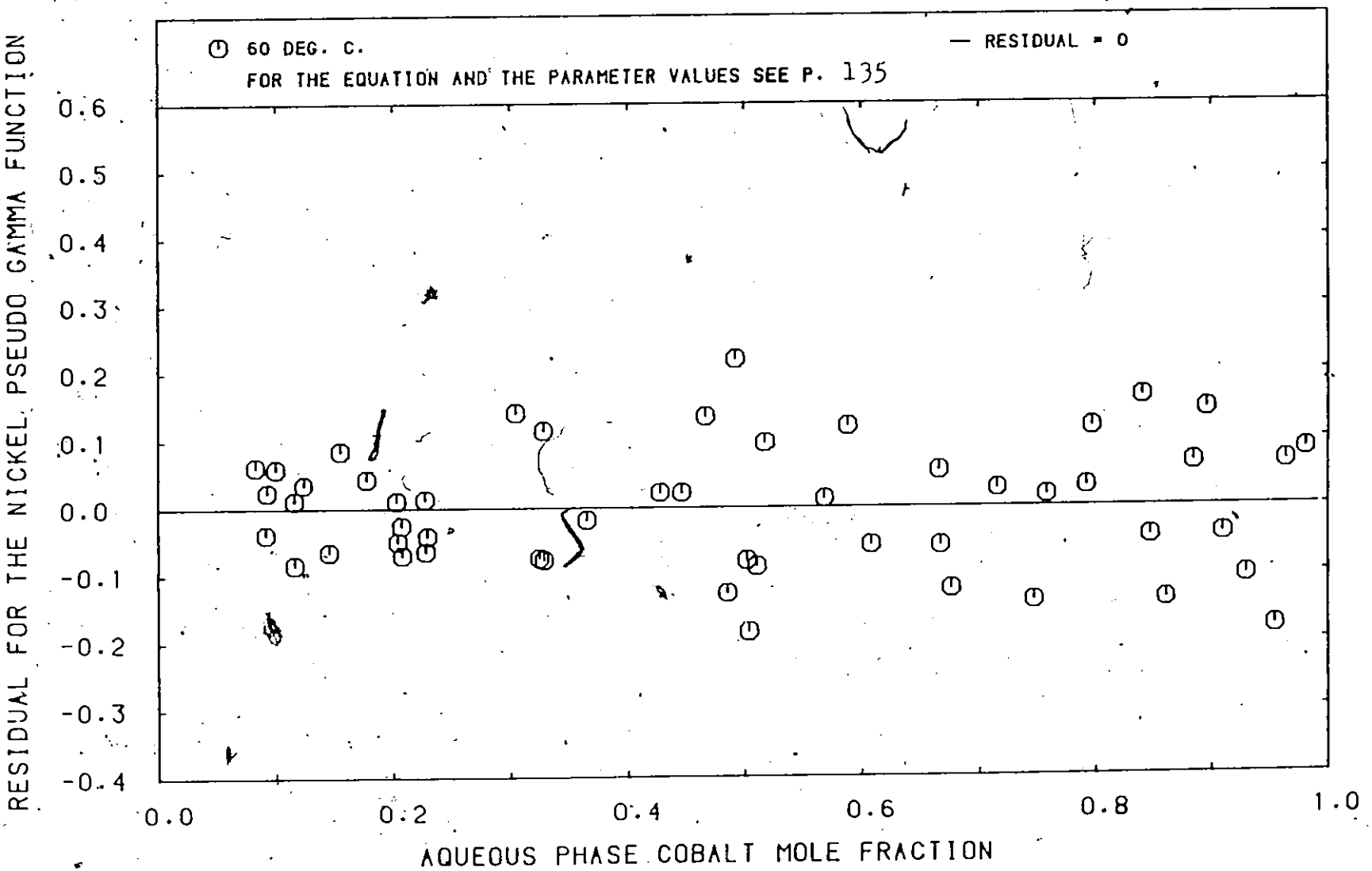


FIGURE 15B2 RESIDUAL PLOT AS A FUNCTION OF AQUEOUS PHASE COBALT MOLE FRACTION FOR THE PSEUDO GAMMA NICKEL FUNCTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

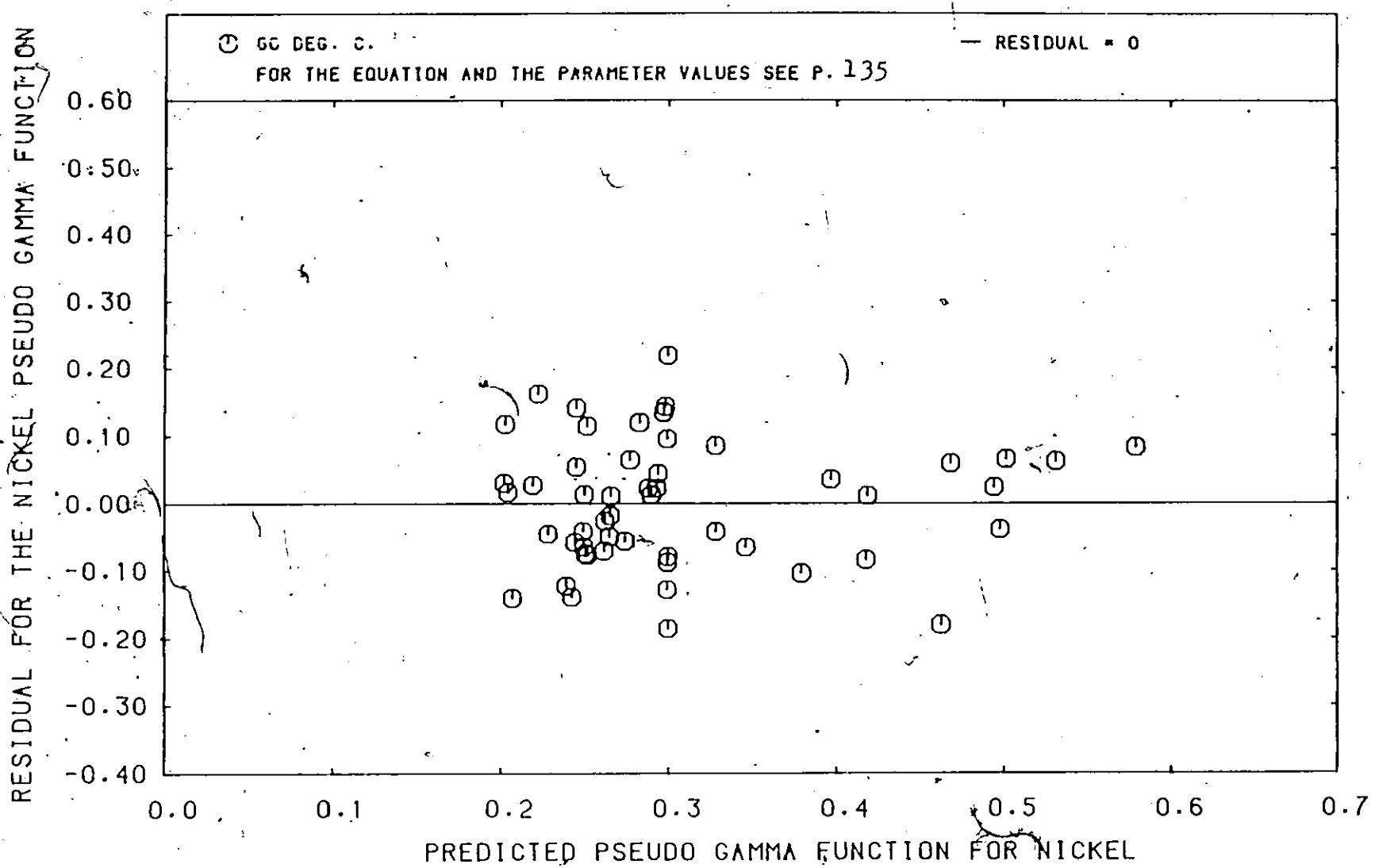


FIGURE 15C2 RESIDUAL PLOT AS A FUNCTION OF THE PREDICTED NICKEL PSEUDO GAMMA FUNCTION AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

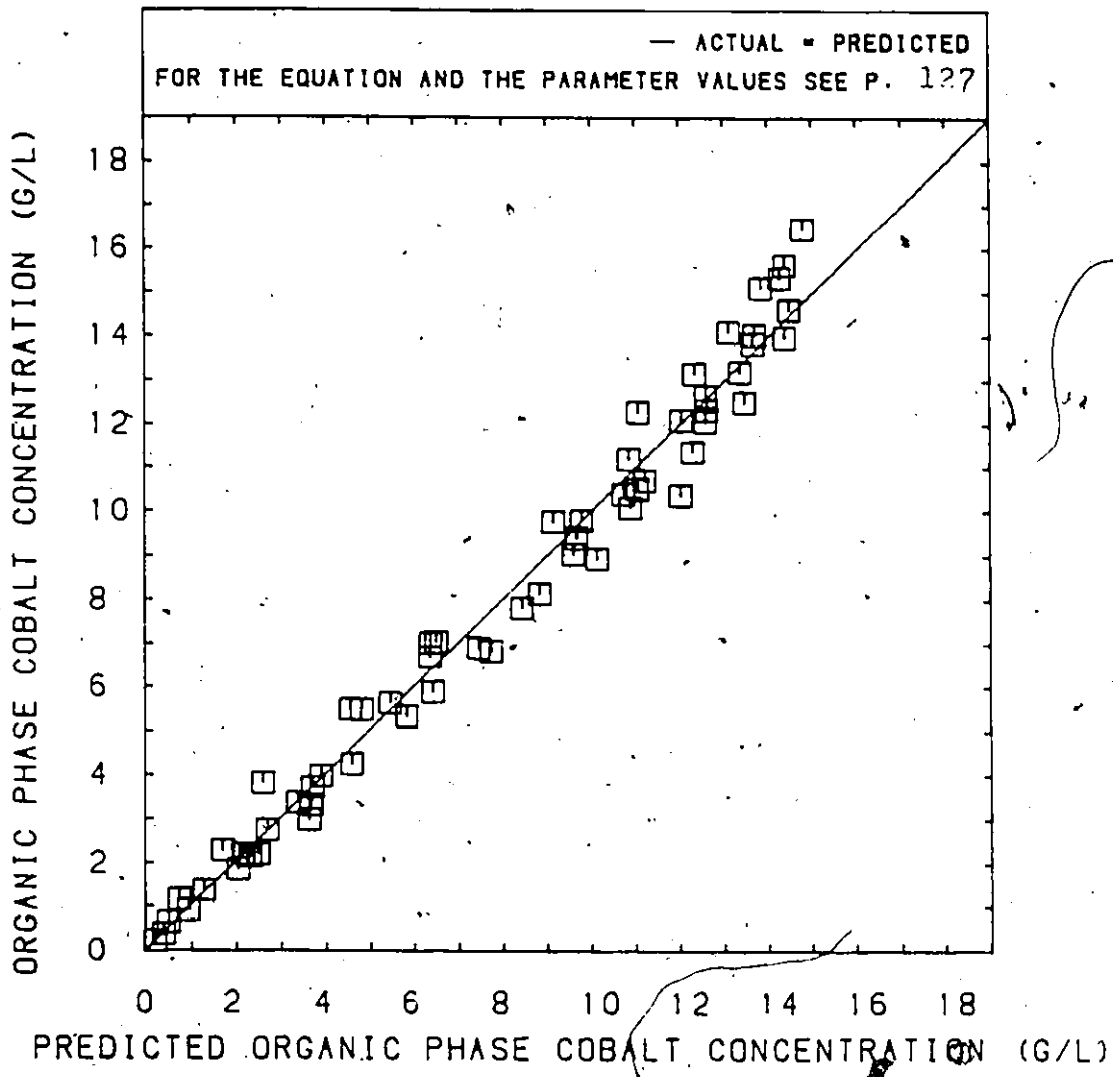


FIGURE 16. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE COBALT CONCENTRATION FOR THE DELTA Y METHOD AT 25 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.3; A/O = 1.

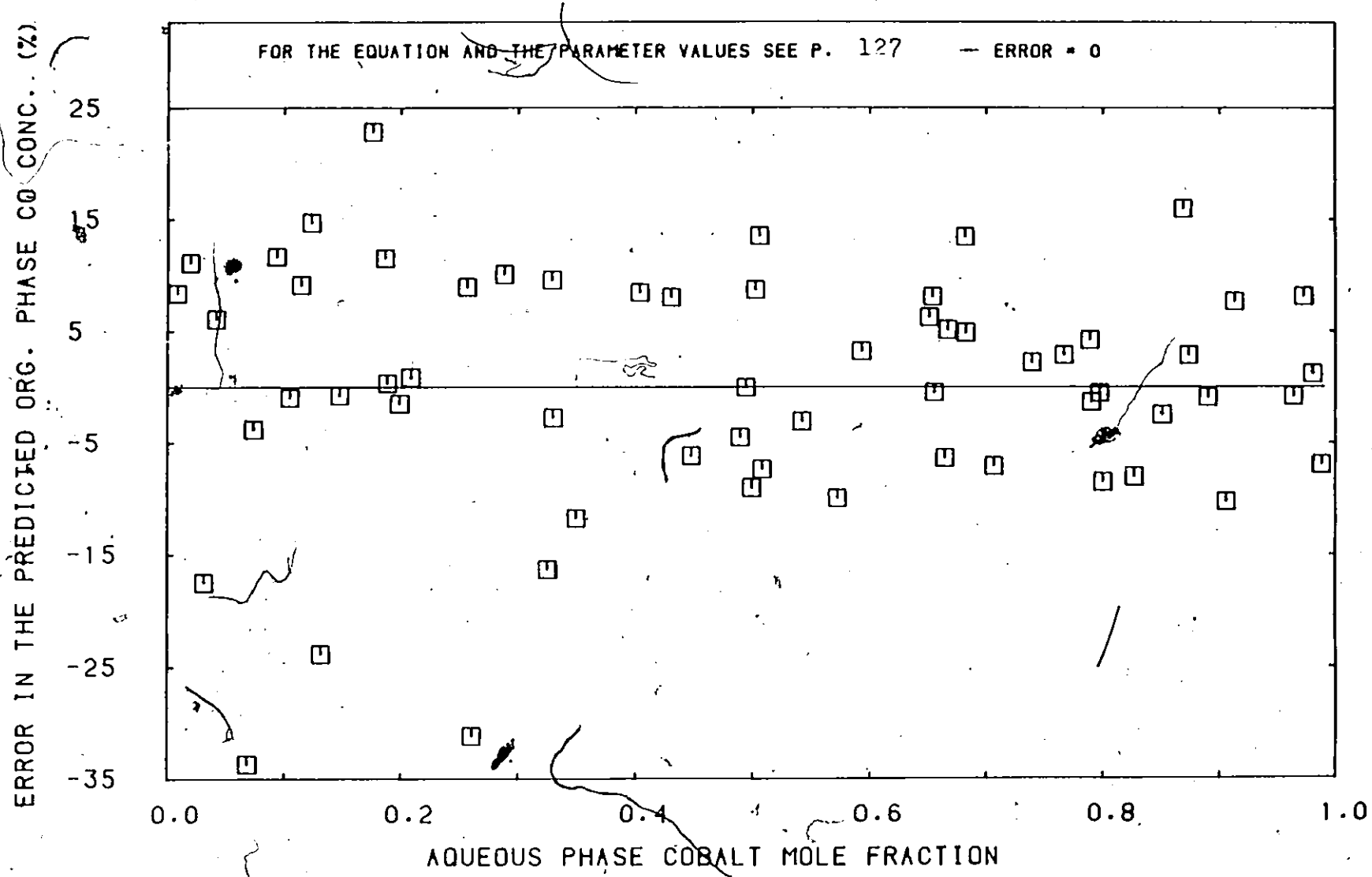


FIGURE 16A. ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE DELTA Y METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL OX 3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

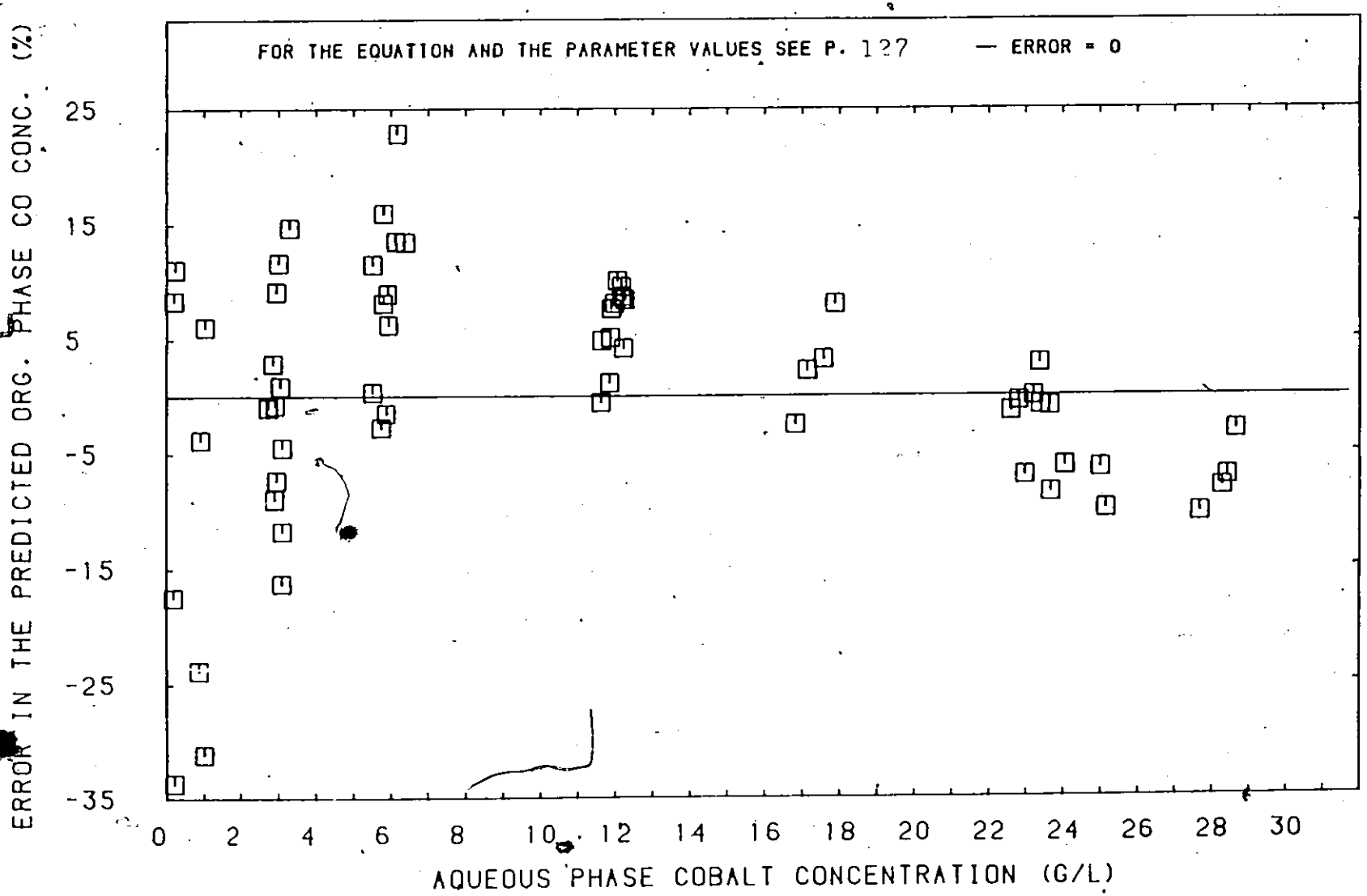


FIGURE 16B.ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE DELTA-Y METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

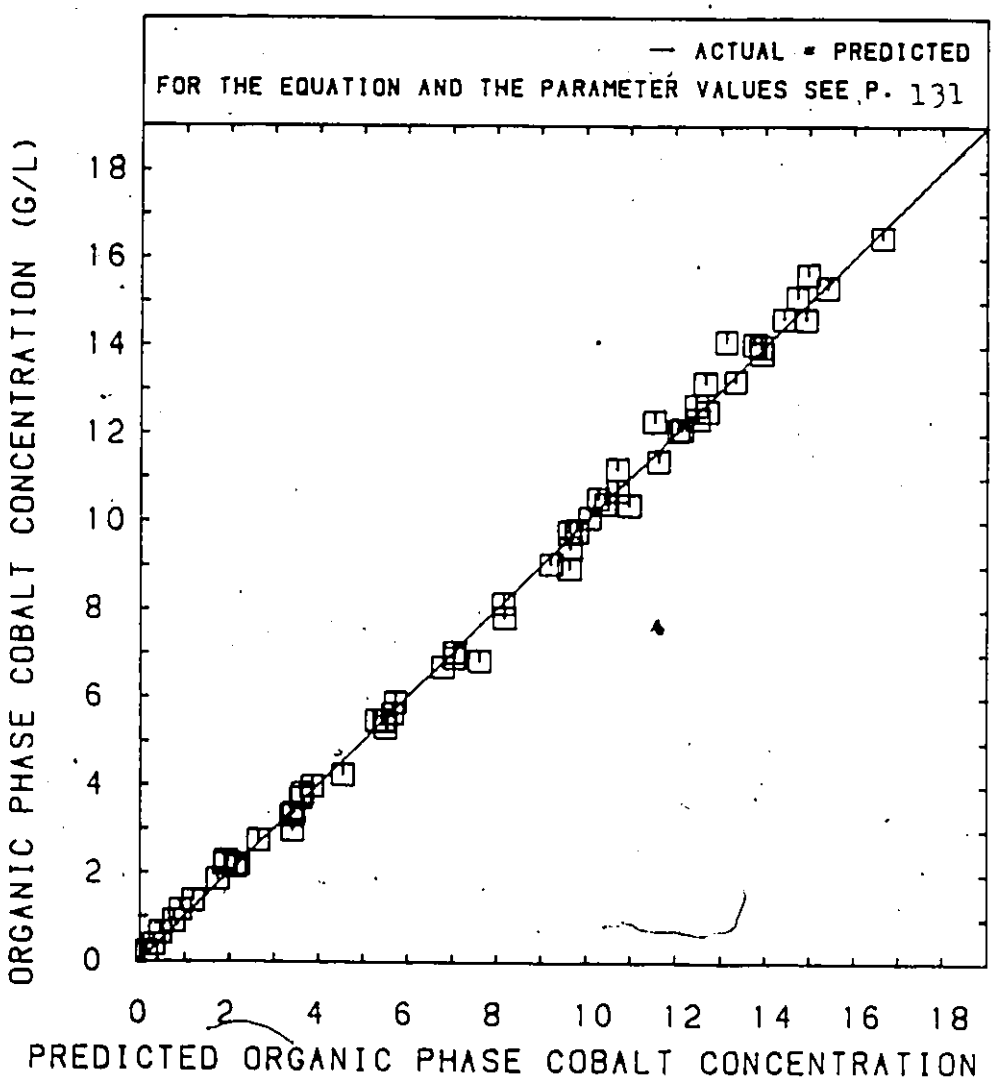


FIGURE 17. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE COBALT CONCENTRATION FOR THE MOLE FRACTION METHOD AT 25 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4,
EQUILIBRIUM PH = 5.3-6.3; A/O = 1.

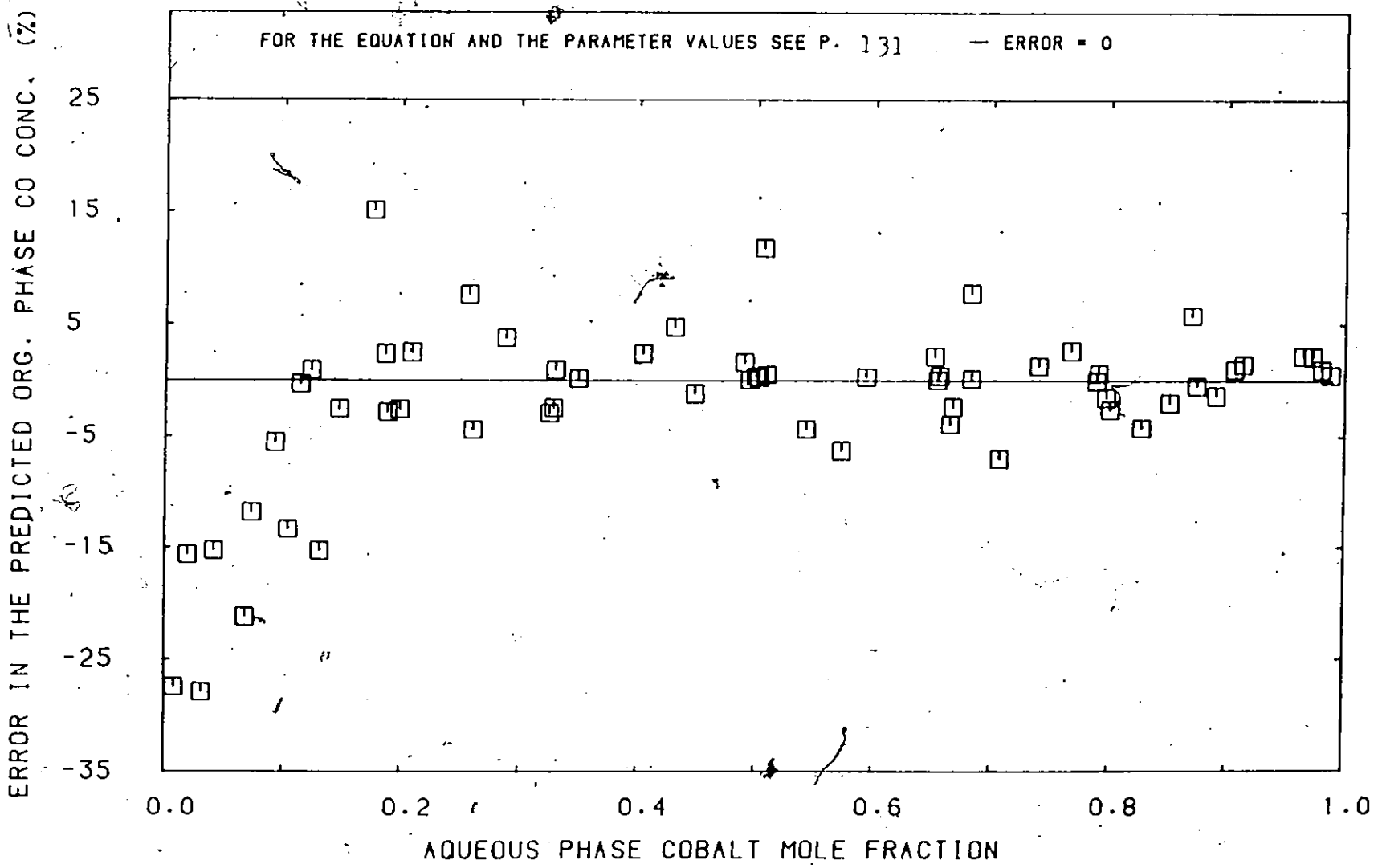


FIGURE 17A. ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE MOLE FRACTION METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

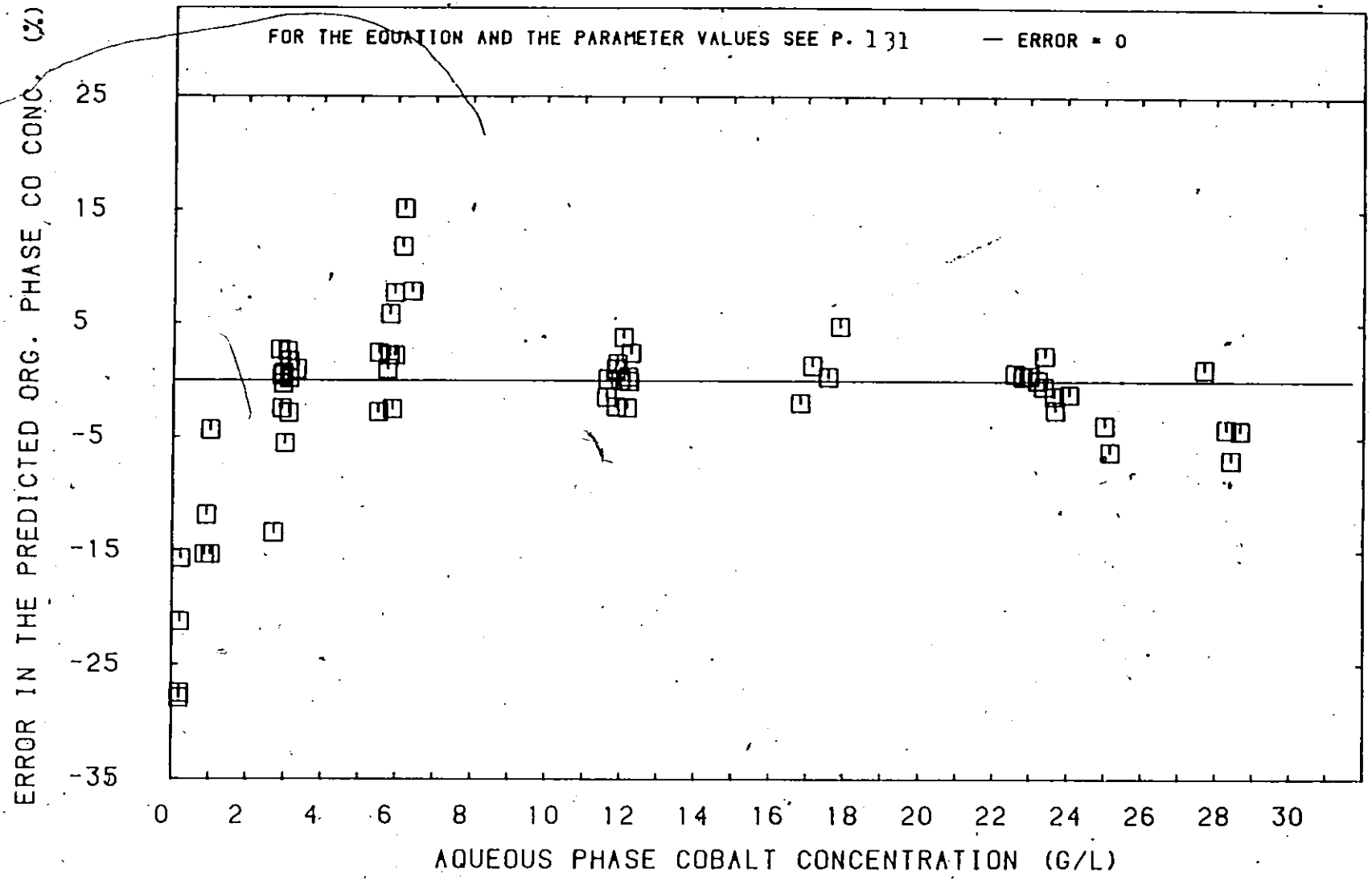


FIGURE 17B. ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE MOLE FRACTION METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

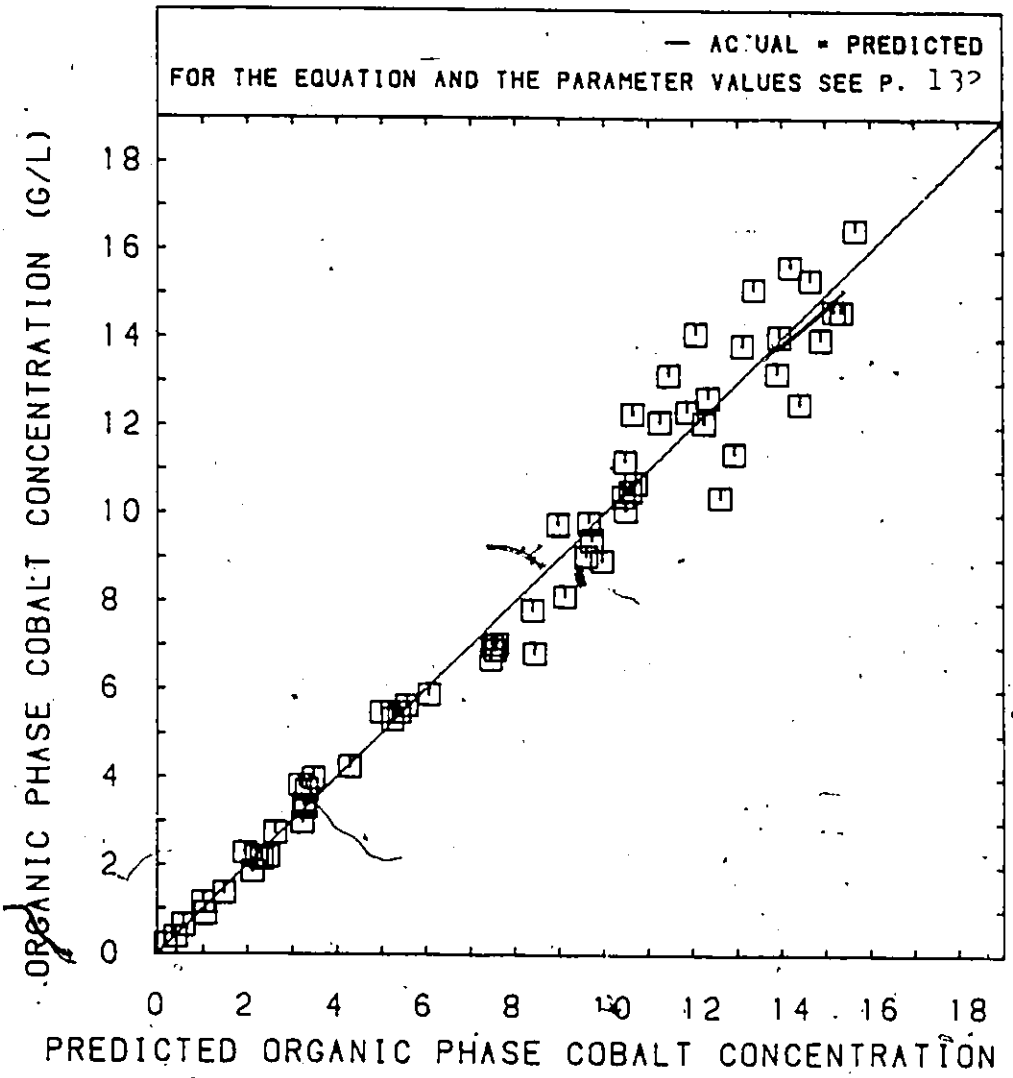


FIGURE 18. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE COBALT CONCENTRATION FOR THE PSEUDO GAMMA METHOD AT 25 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4,
EQUILIBRIUM PH = 5.3-6.3; A/O = 1.

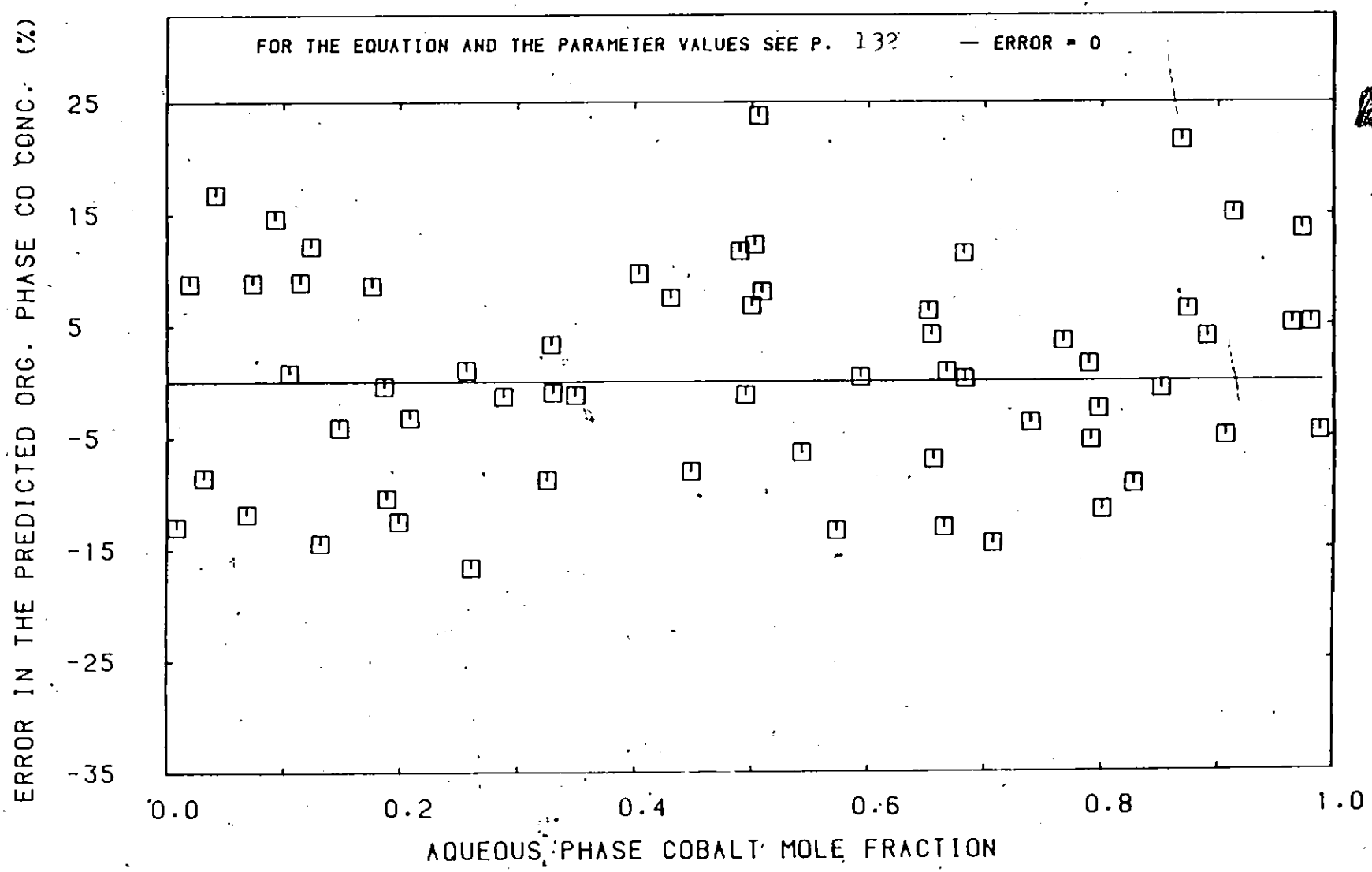


FIGURE 18A. ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE PSEUDO GAMMA METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

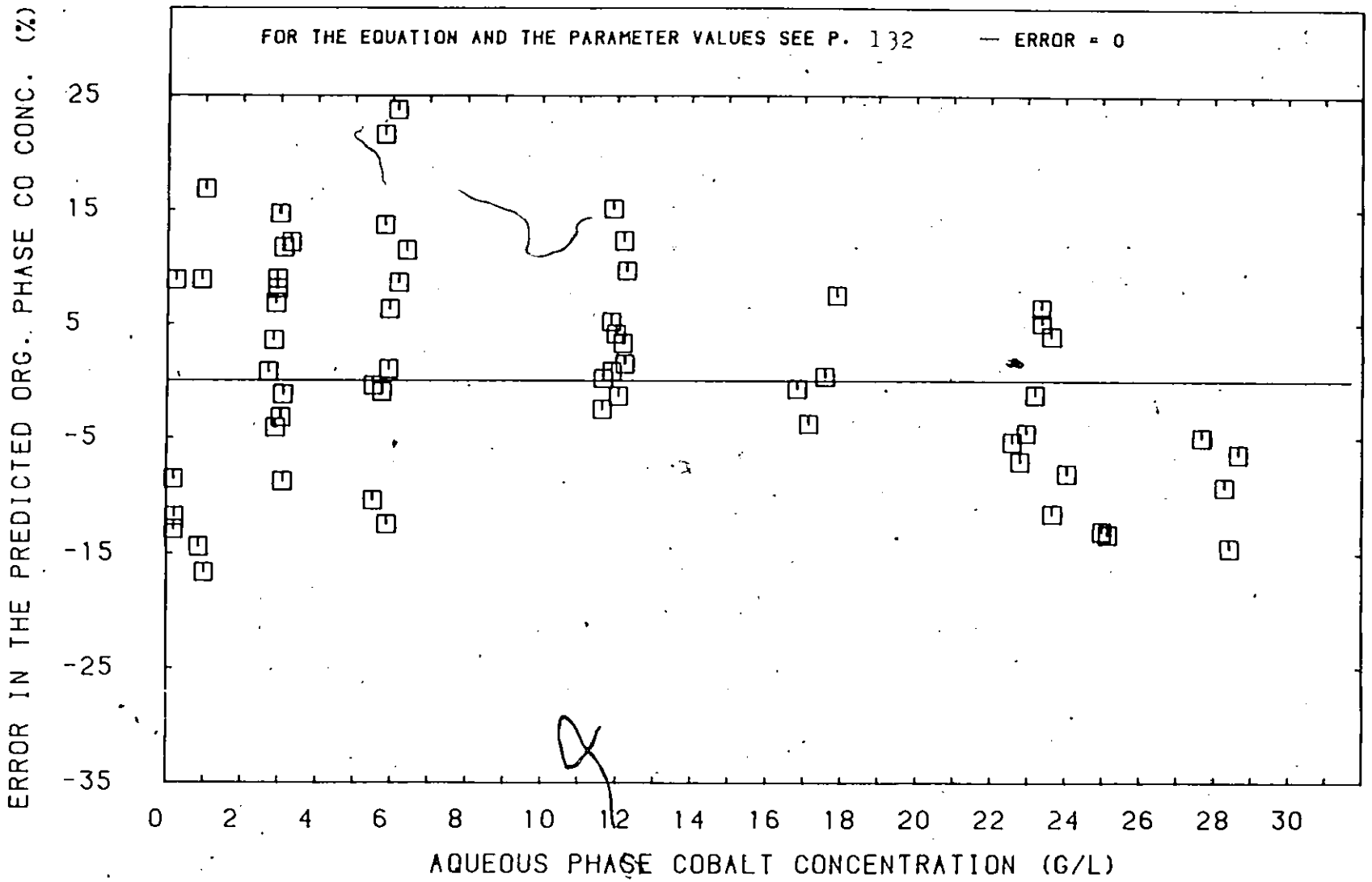


FIGURE18B. ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE PSEUDO GAMMA METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

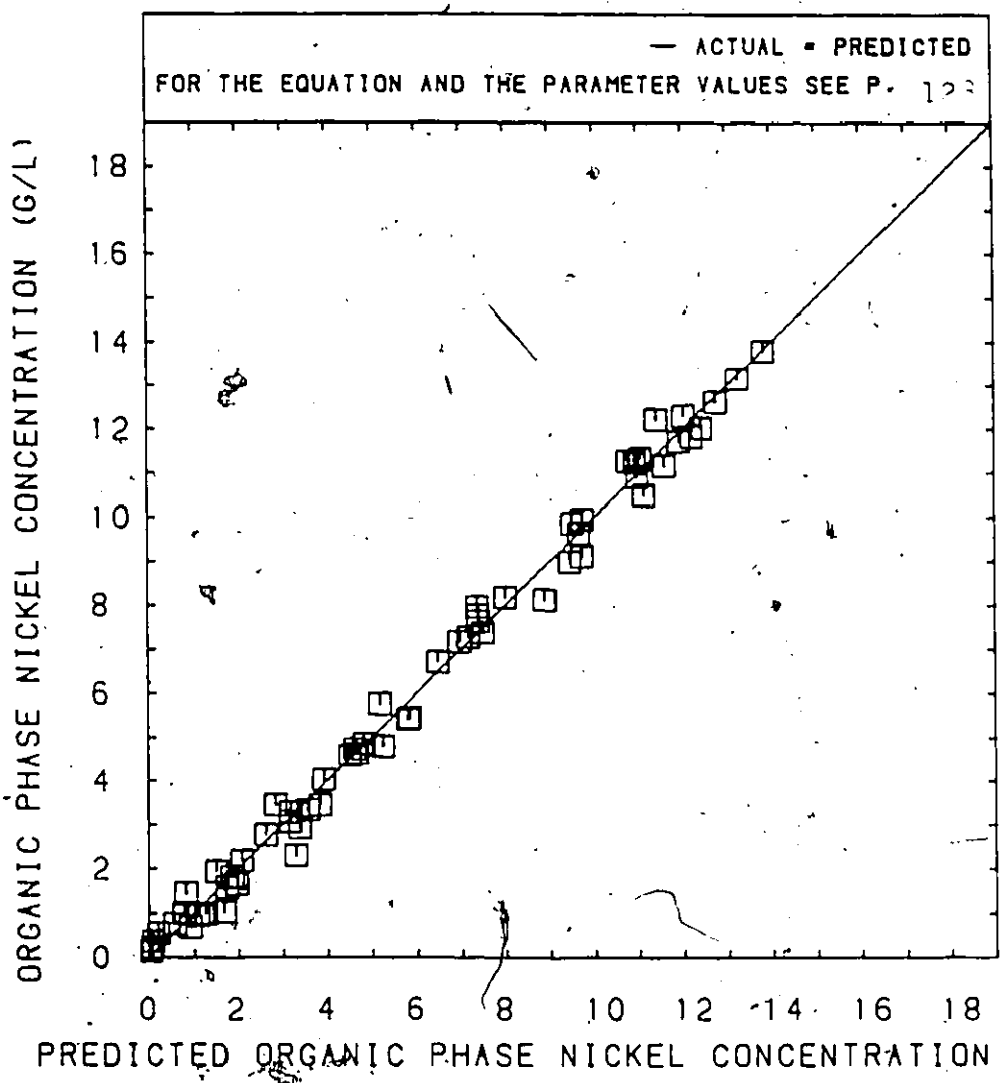


FIGURE 19. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE NICKEL CONCENTRATION FOR THE DELTA Y METHOD AT 25 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4,
EQUILIBRIUM PH = 5.3-6.4, A/O = 1.

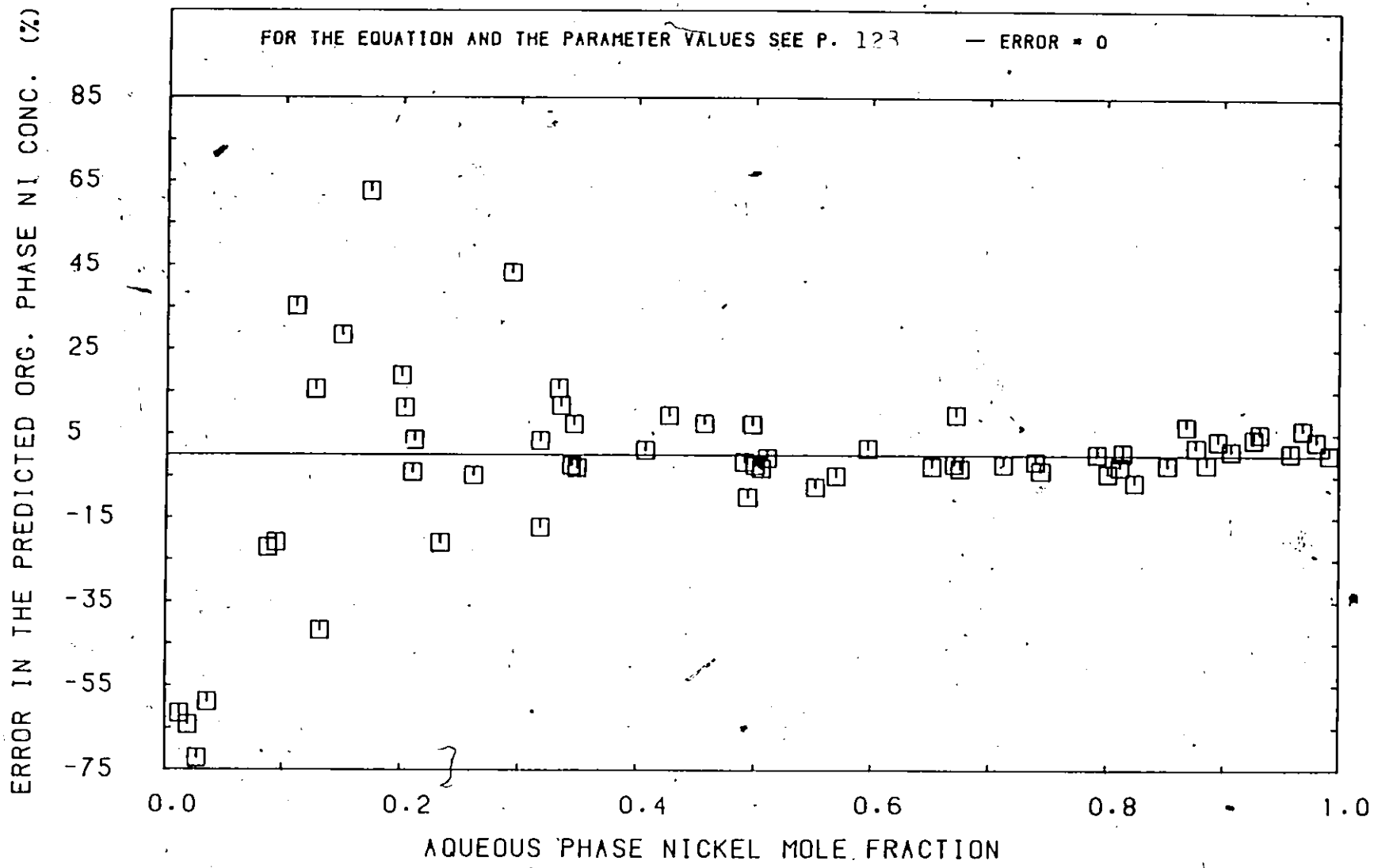


FIGURE 19A. ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE DELTA Y METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

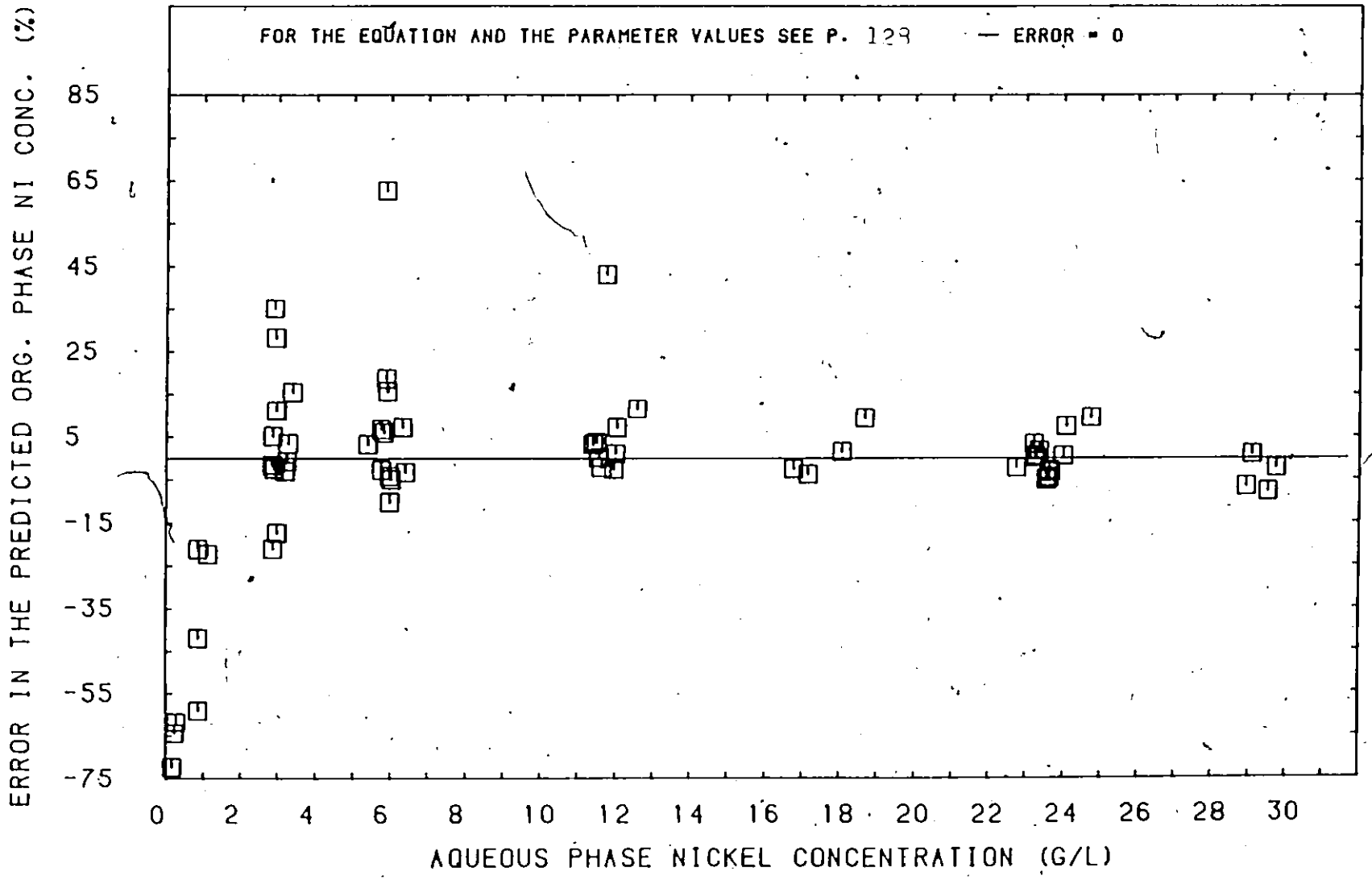


FIGURE 19B. ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE DELTA Y METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

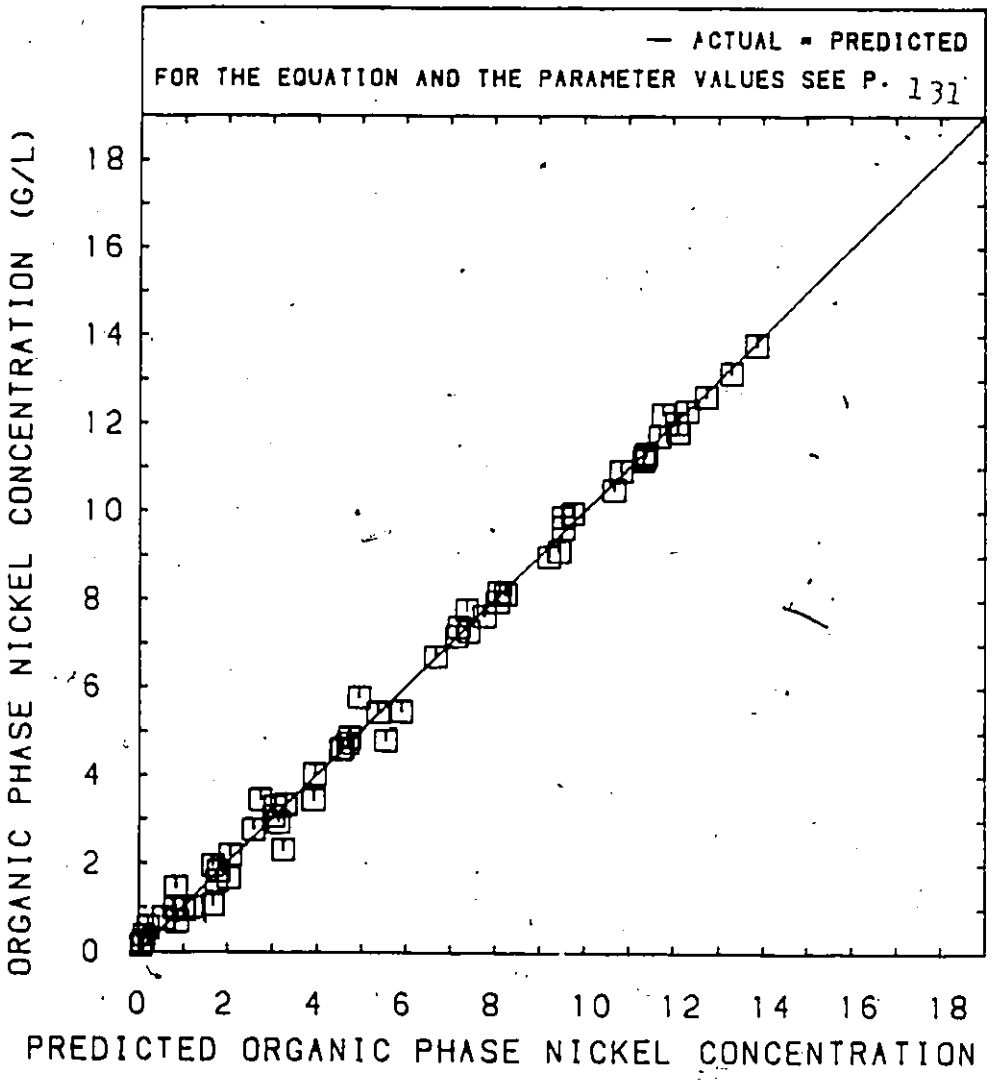


FIGURE 20. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE NICKEL CONCENTRATION FOR THE MOLE FRACTION METHOD AT 25 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.4; A/O = 1.

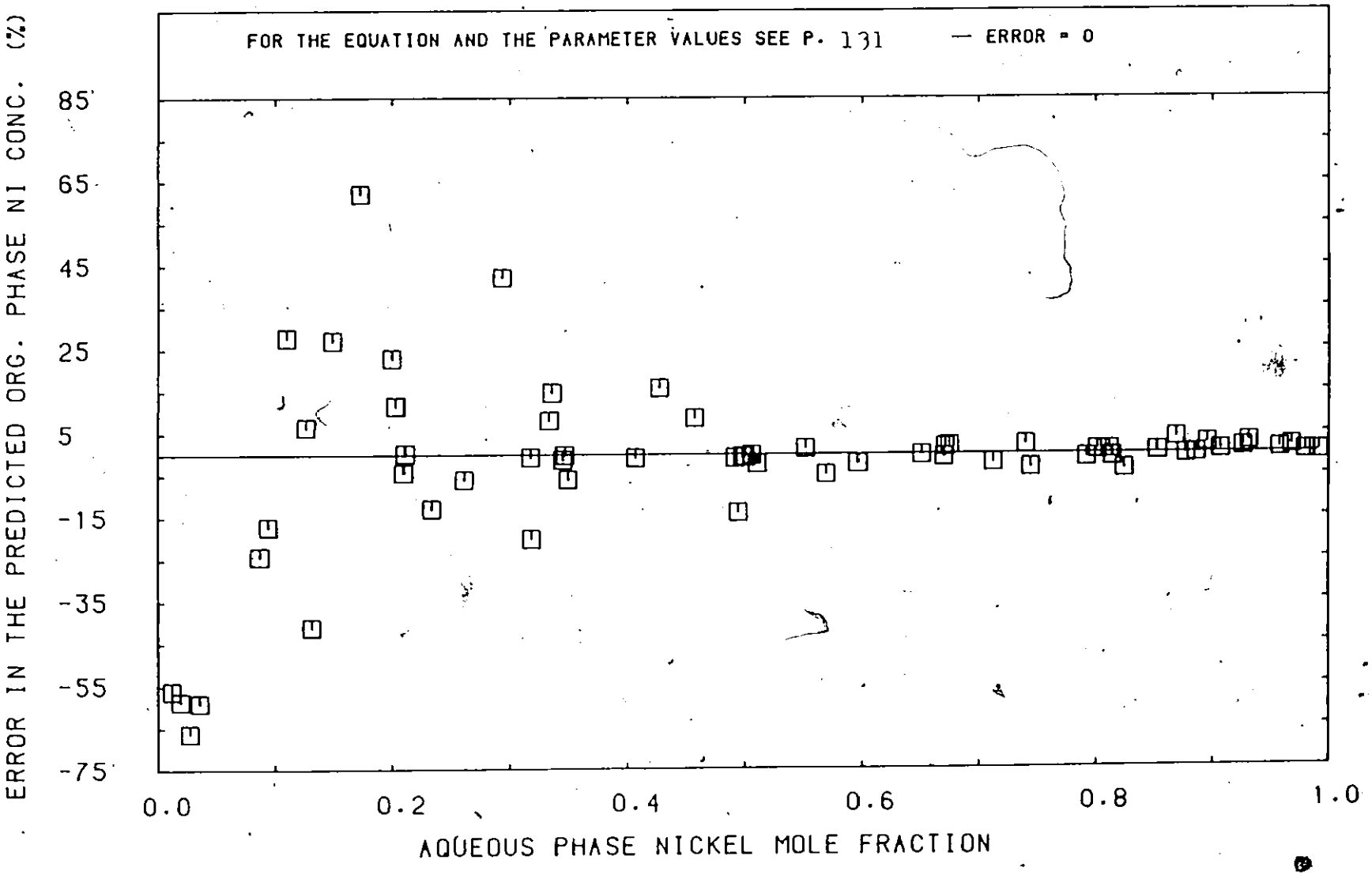


FIGURE 20A: ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE MOLE FRACTION METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

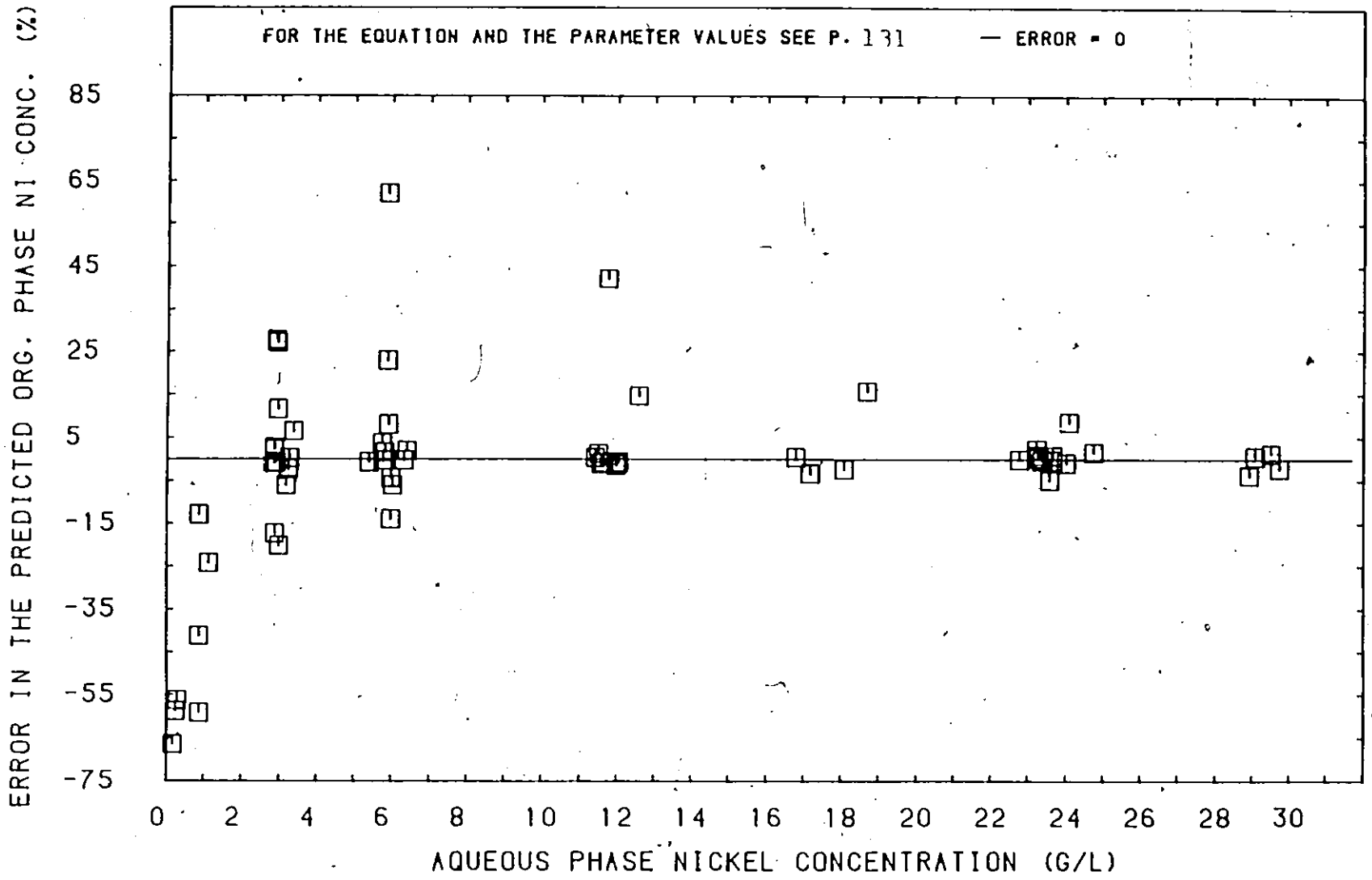


FIGURE 20B. ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE MOLE FRACTION METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

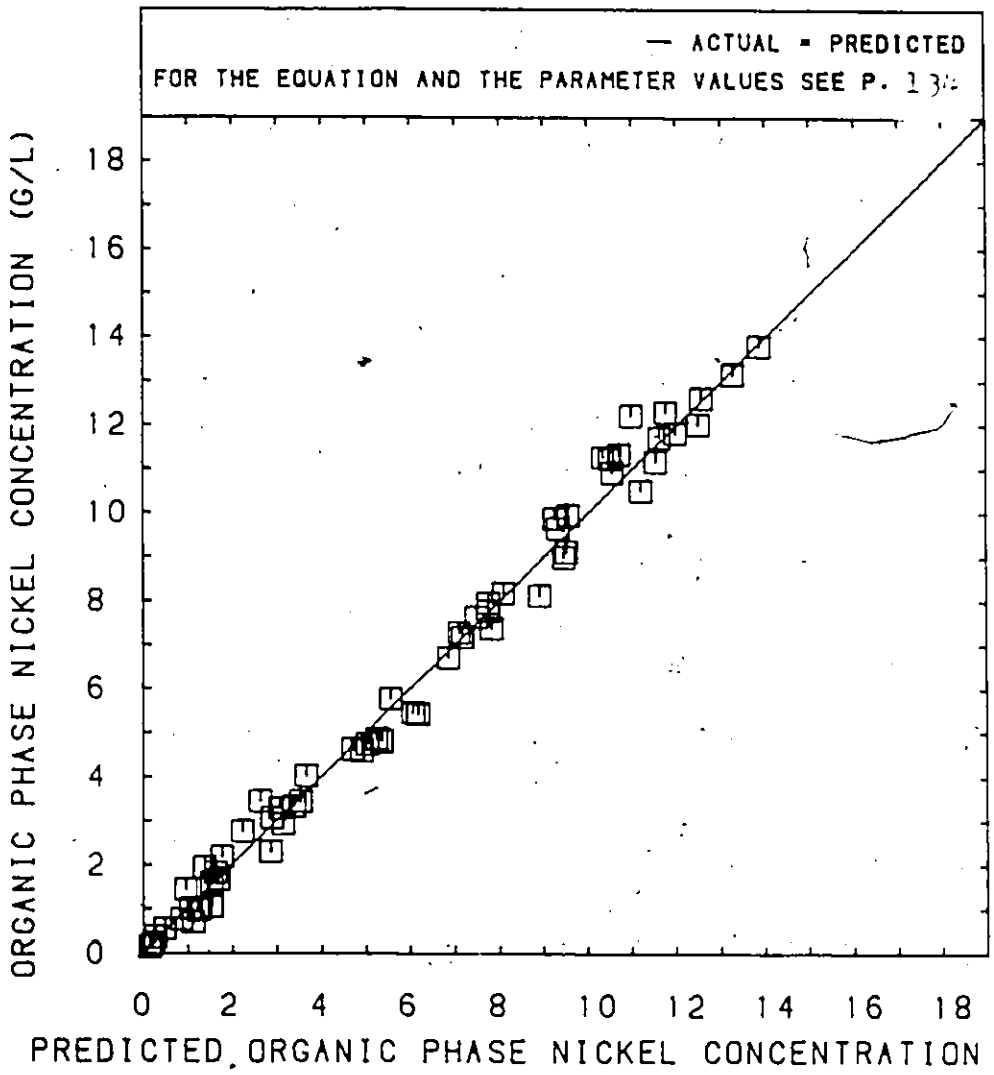


FIGURE 21. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE NICKEL CONCENTRATION FOR THE PSEUDO GAMMA METHOD AT 25 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.3-6.4; A/O = 1.

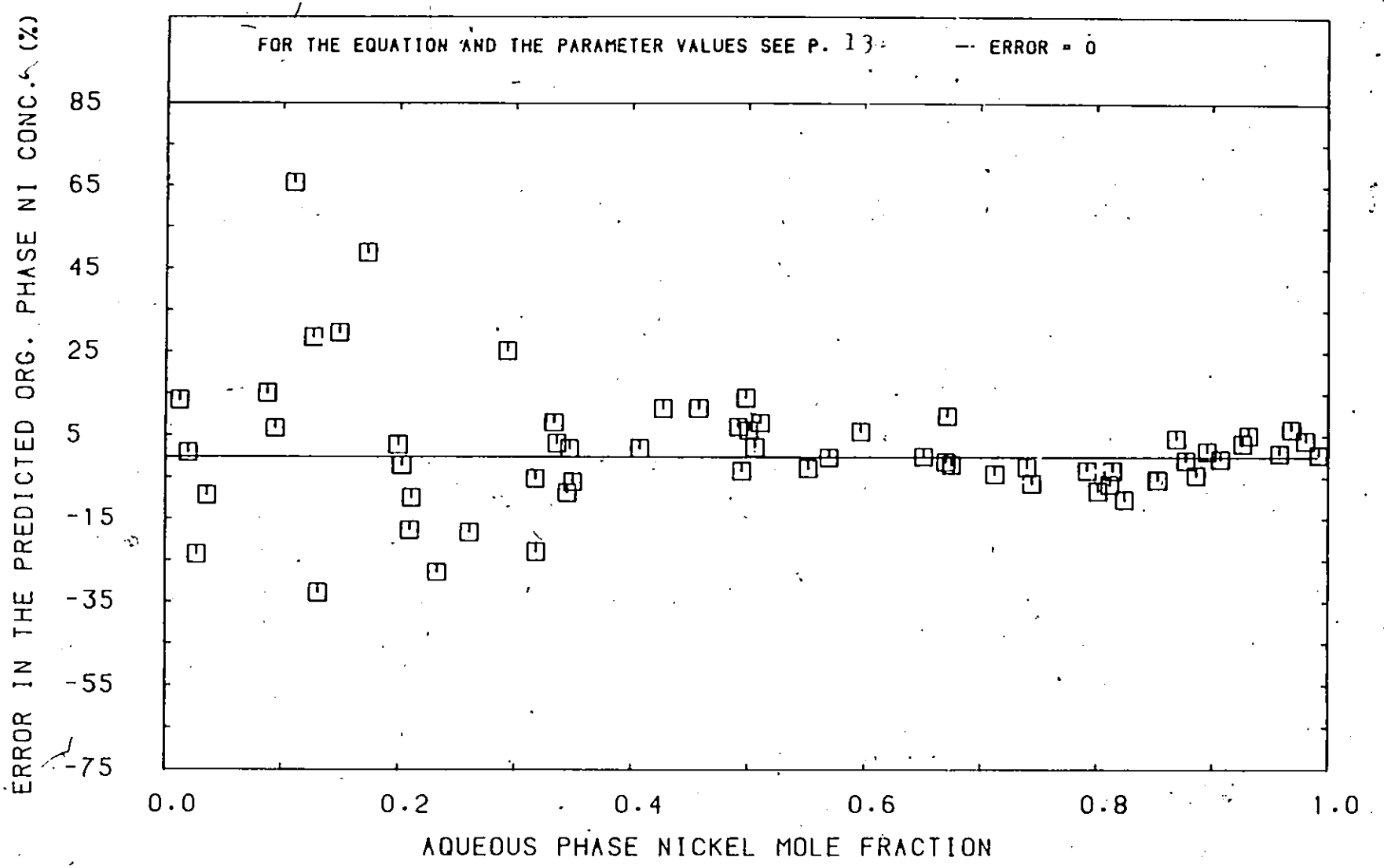


FIGURE 21A. ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE PSEUDO GAMMA METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.3-6.4.

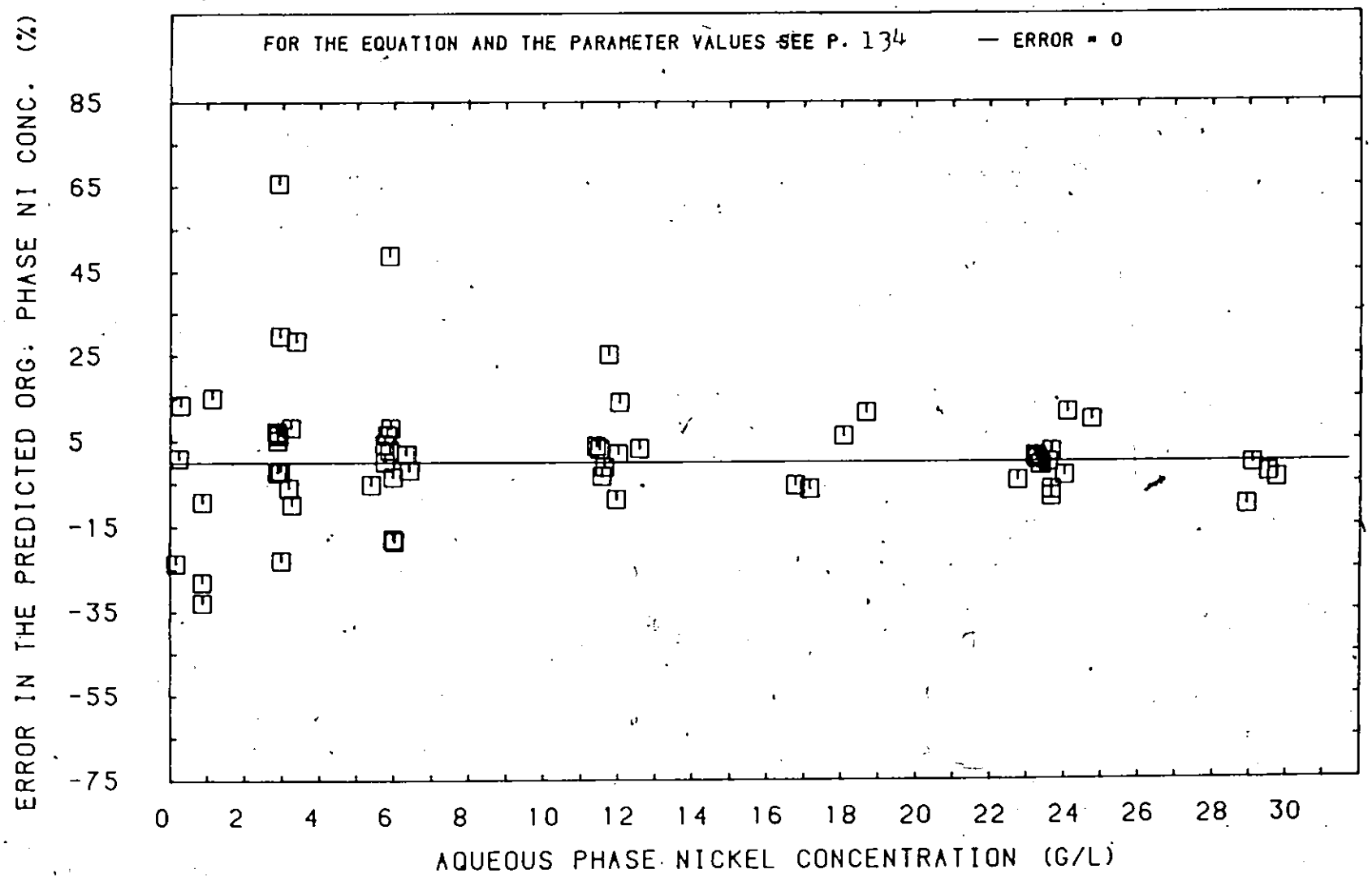


FIGURE 21B. ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE PSEUDO GAMMA METHOD AT 25 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.3-6.4.

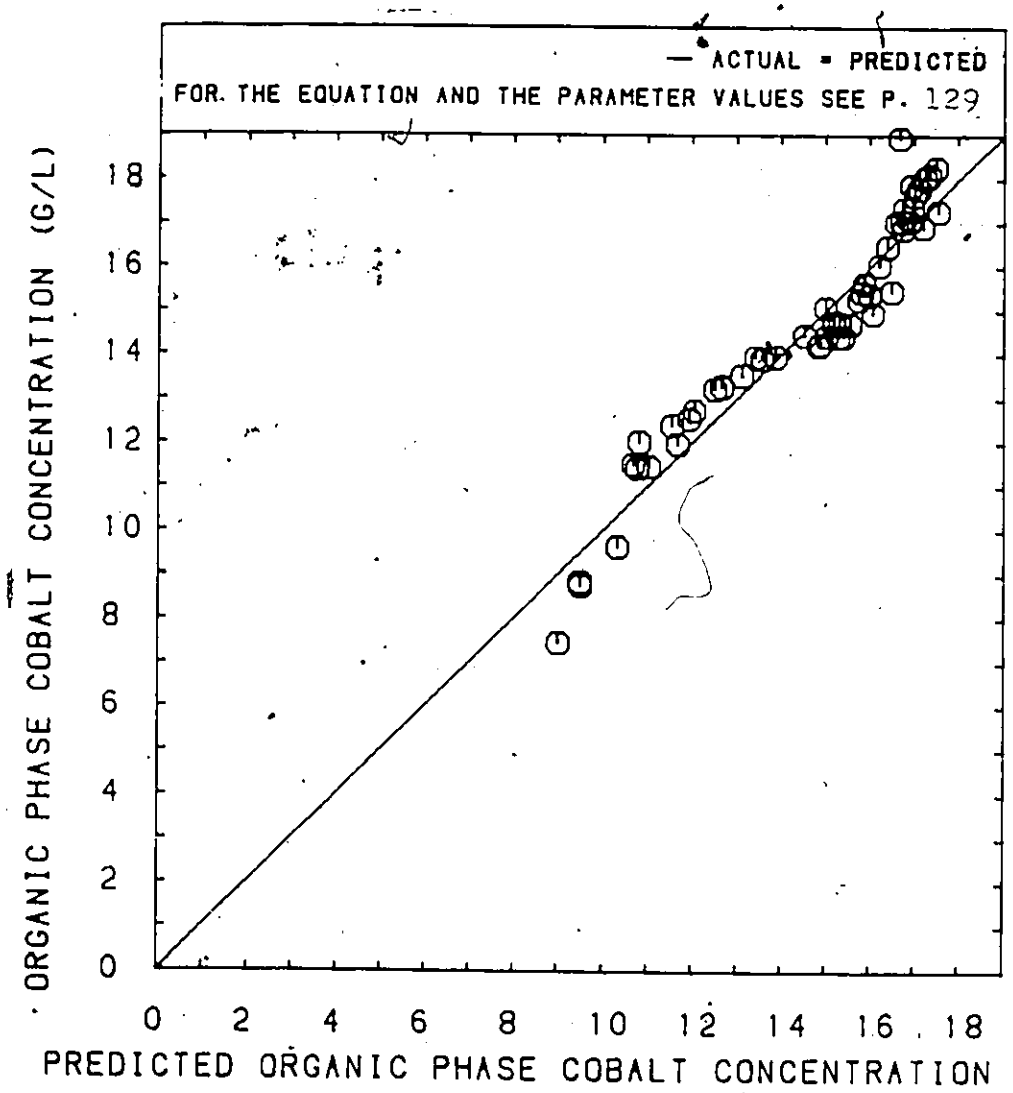


FIGURE 22. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE COBALT CONCENTRATION FOR THE DELTA Y METHOD AT 60 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.5-6.4; A/O = 1.

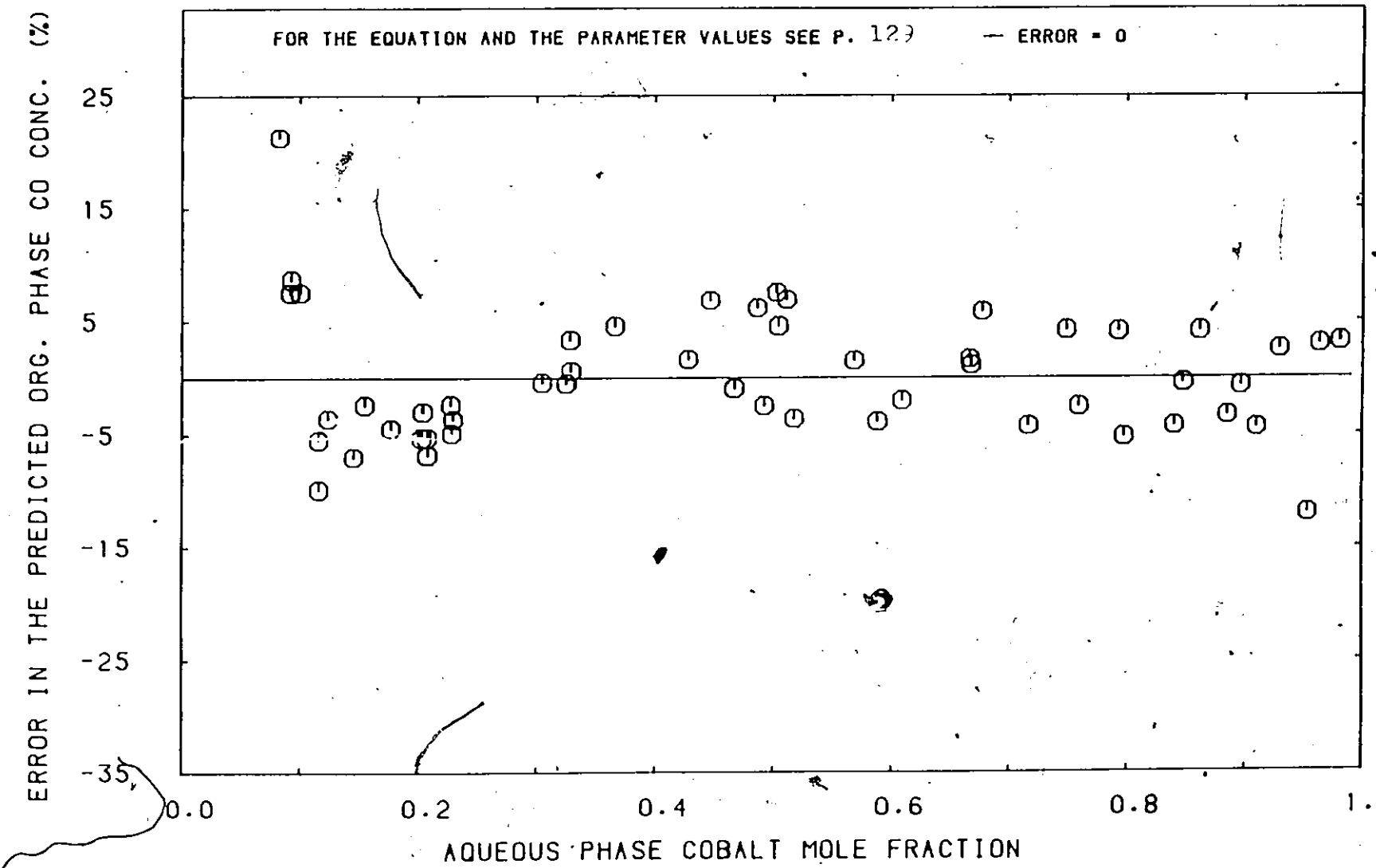


FIGURE 22A. ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE DELTA K METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

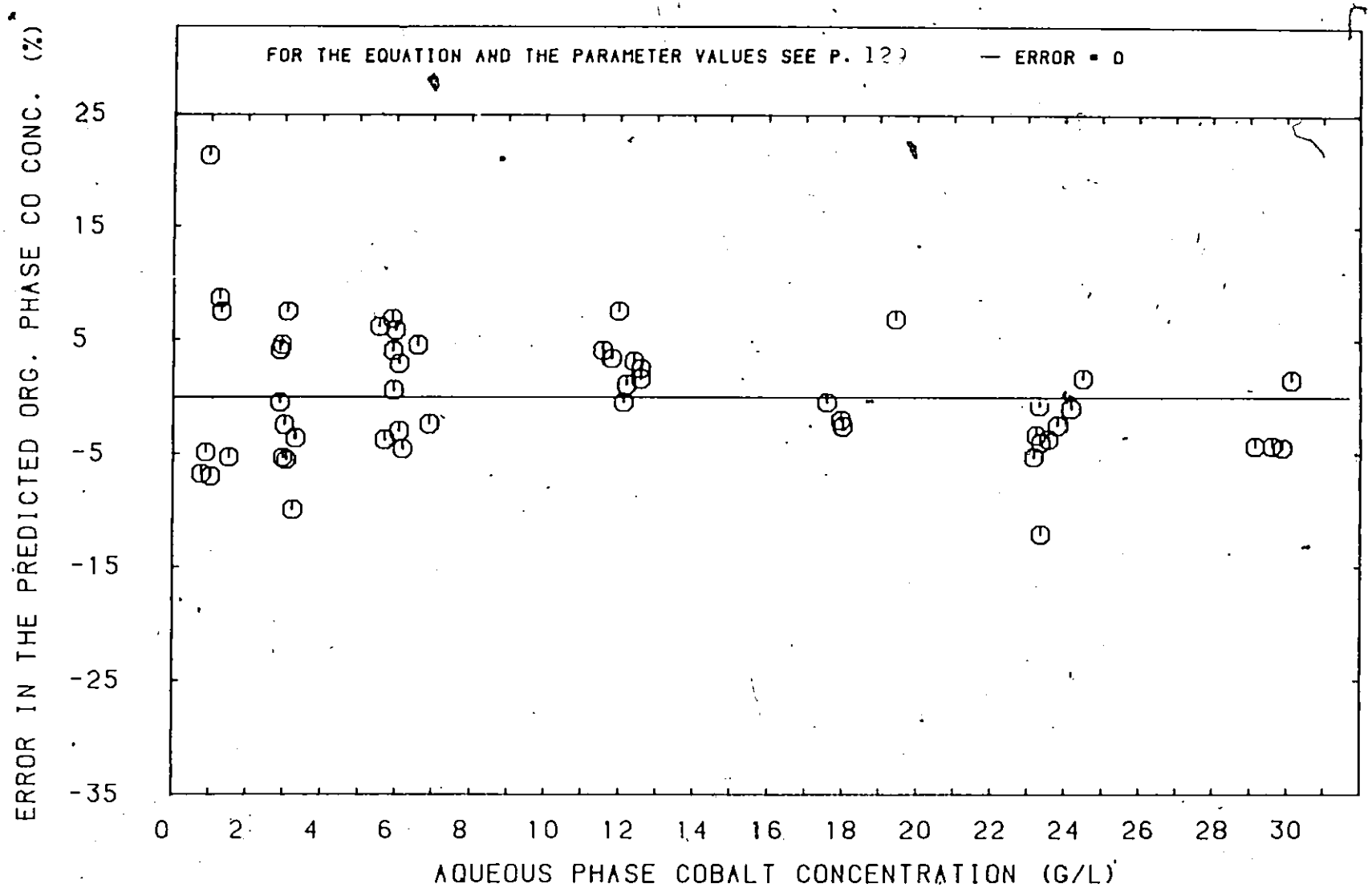


FIGURE 22B. ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE DELTA Y METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP: A/O = 1.

AQUEOUS PHASE: 20.G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

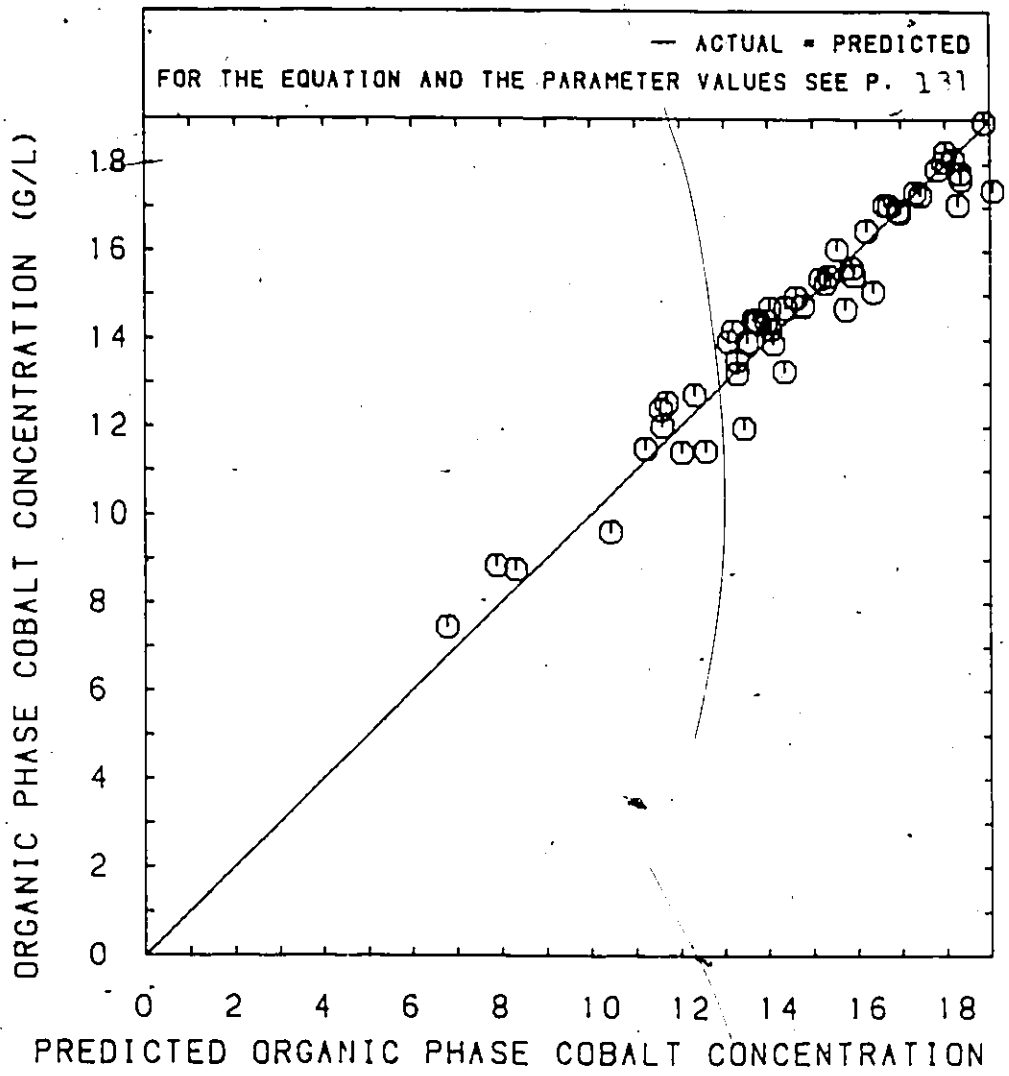


FIGURE 23. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE COBALT CONCENTRATION FOR THE MOLE FRACTION METHOD AT 60 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.5-6.4; A/O = 1.

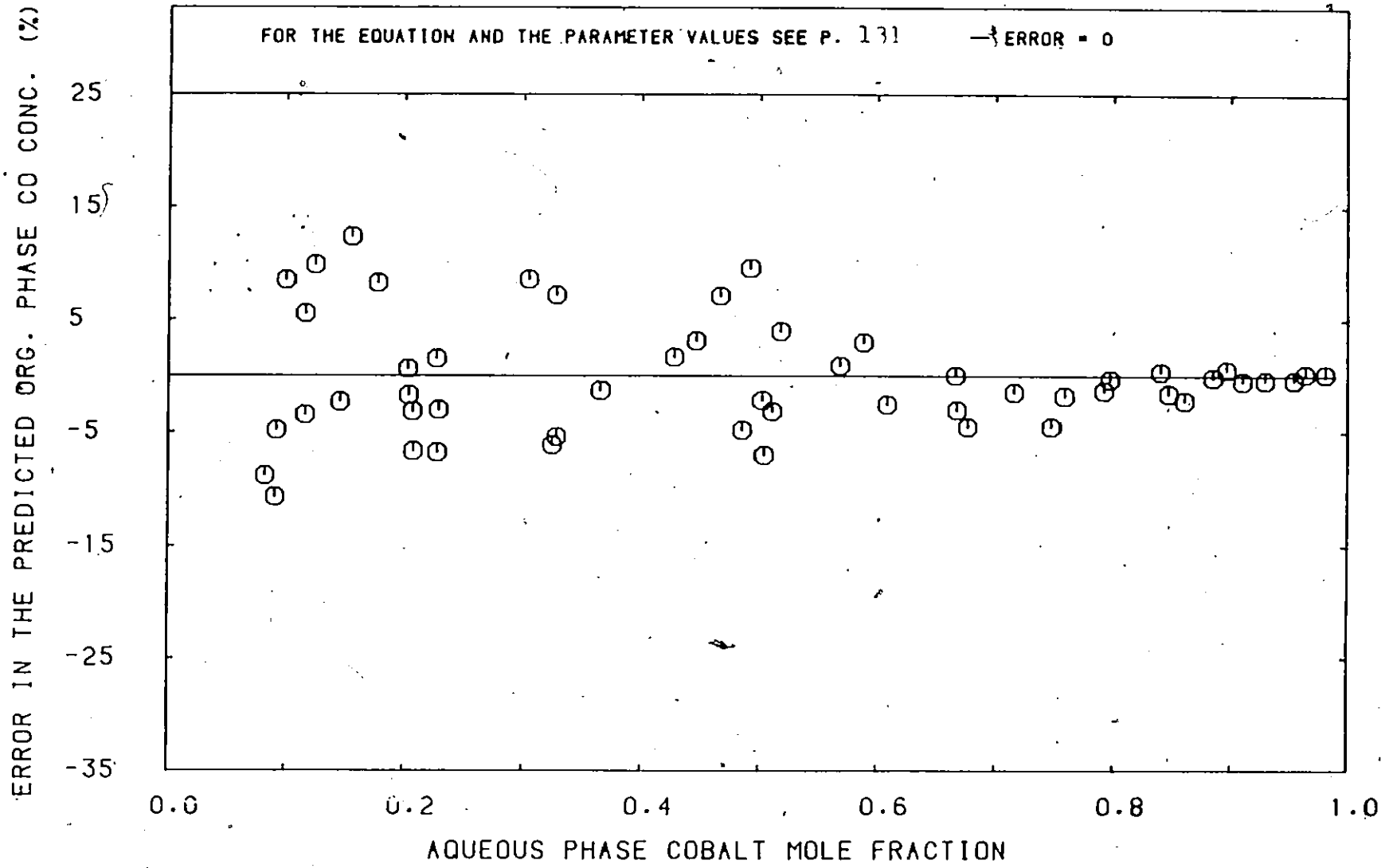


FIGURE 23A. ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE MOLE FRACTION METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

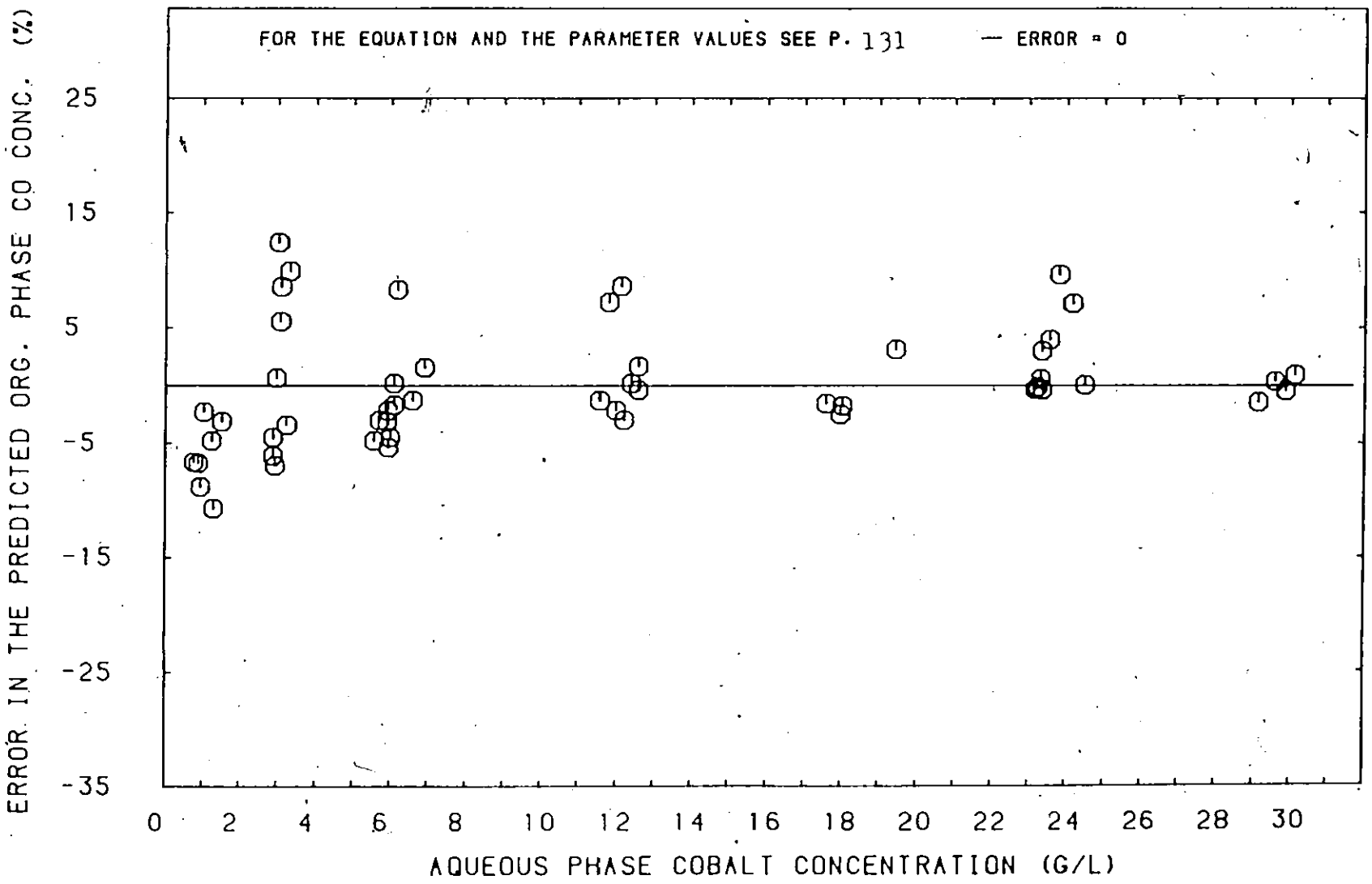


FIGURE 33. ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE MOLE FRACTION METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

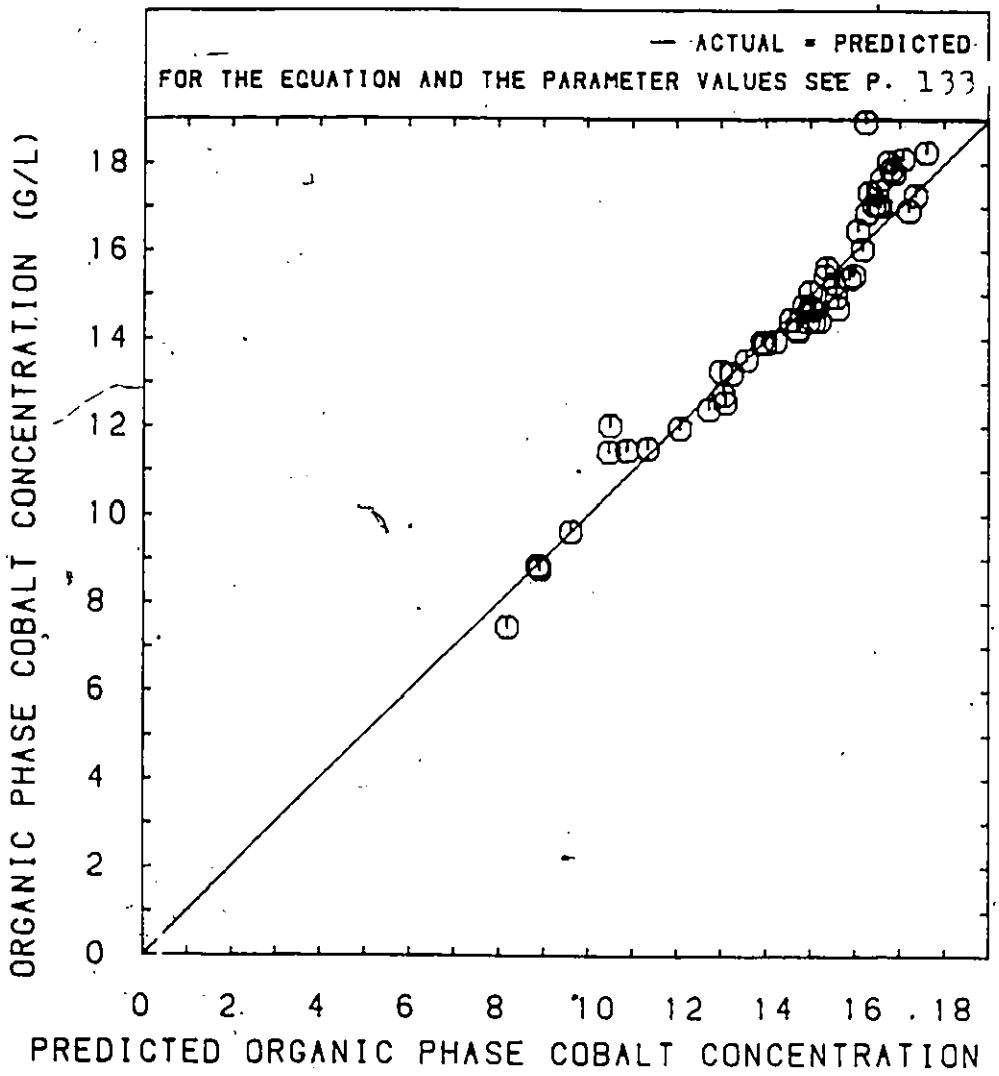


FIGURE 24. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE COBALT CONCENTRATION FOR THE PSEUDO GAMMA METHOD AT 60 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP.
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4,
EQUILIBRIUM PH. = 5.5-6.4; A/O = 1.

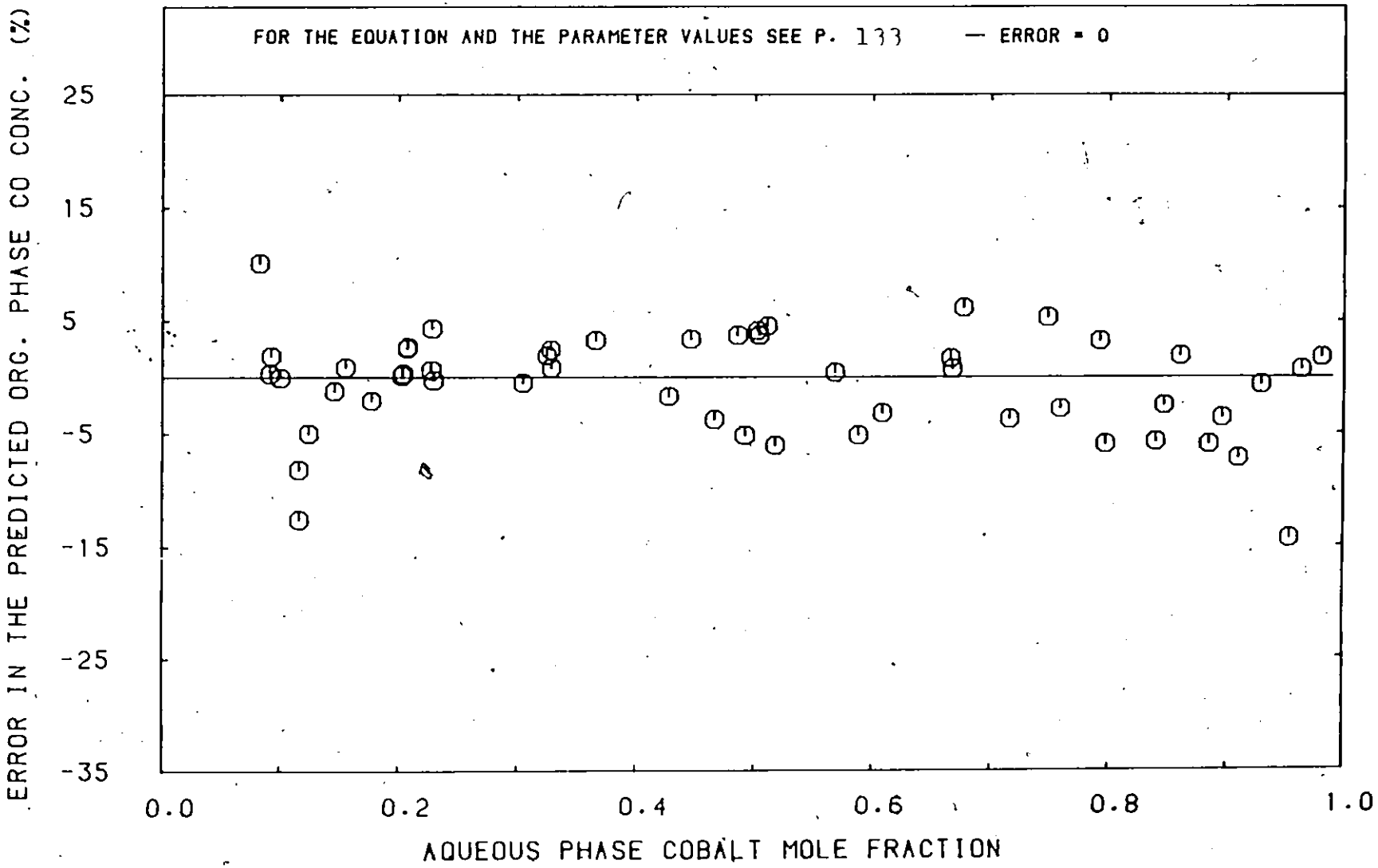


FIGURE 24A. ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE PSEUDO GAMMA METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

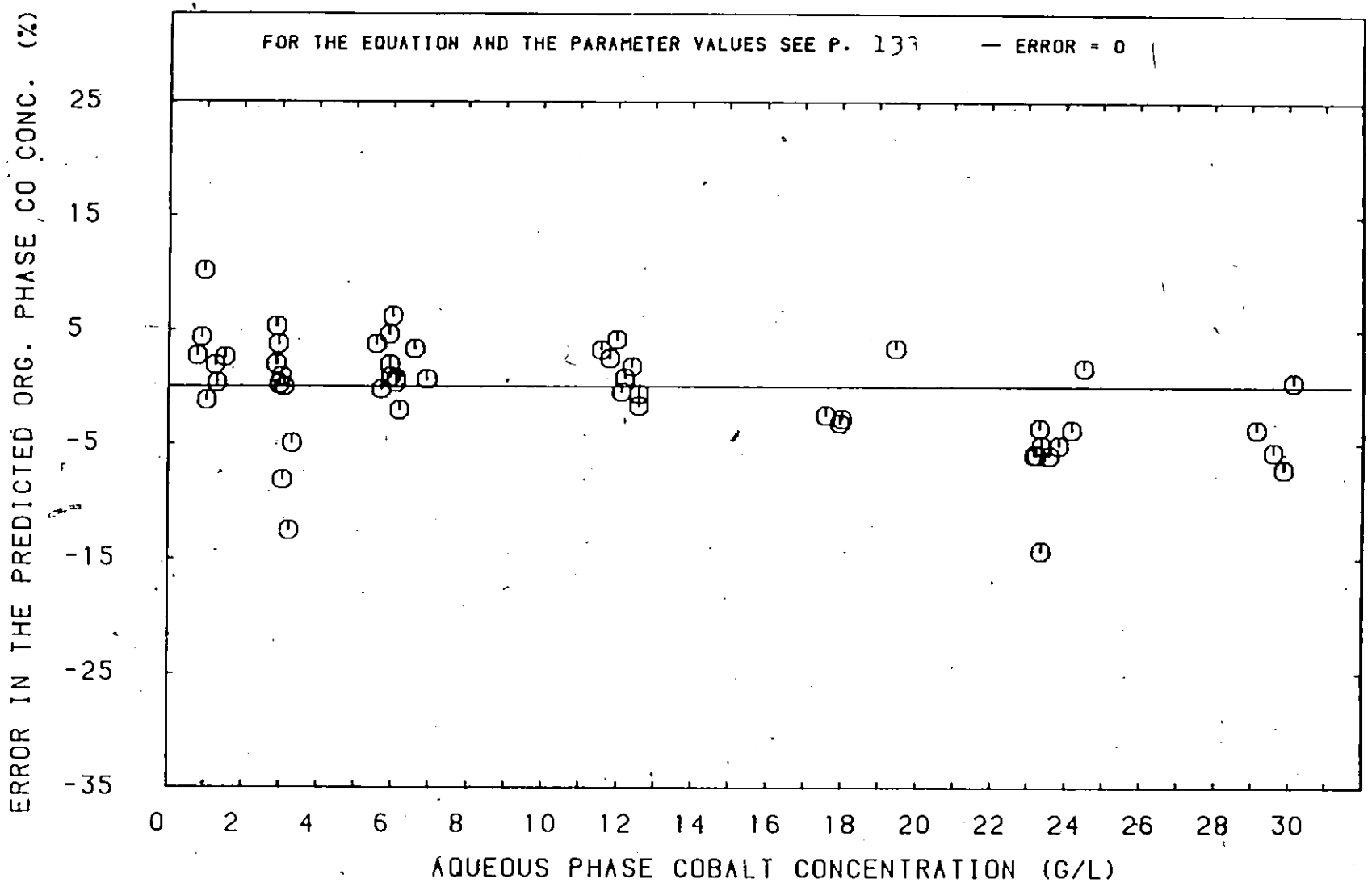


FIGURE 24B. ERROR IN THE PREDICTION OF THE ORGANIC PHASE COBALT CONCENTRATION WITH THE PSEUDO GAMMA METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

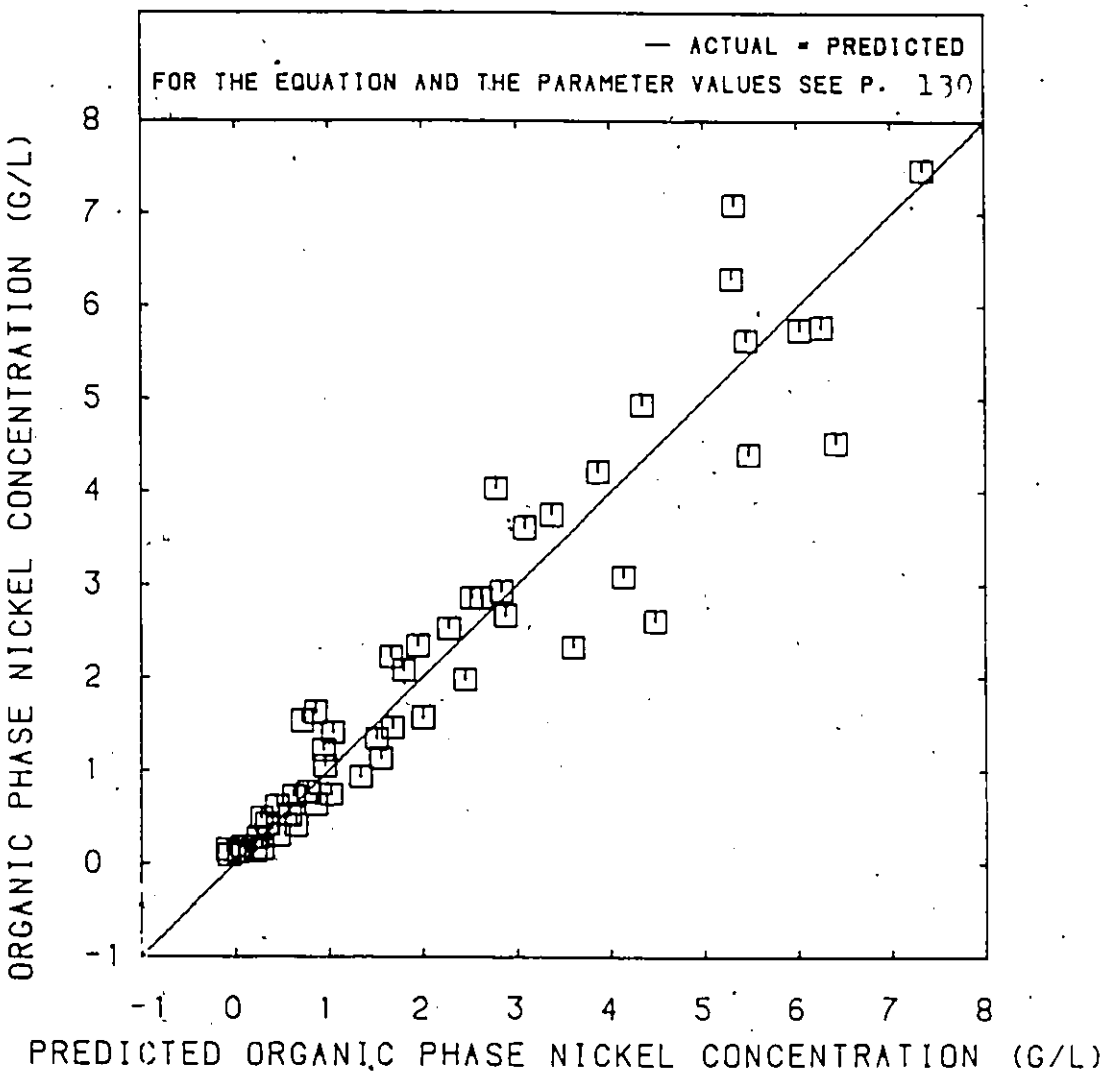


FIGURE 25. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE NICKEL CONCENTRATION FOR THE DELTA Y METHOD AT 60 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.5-6.3; A/O = 1.

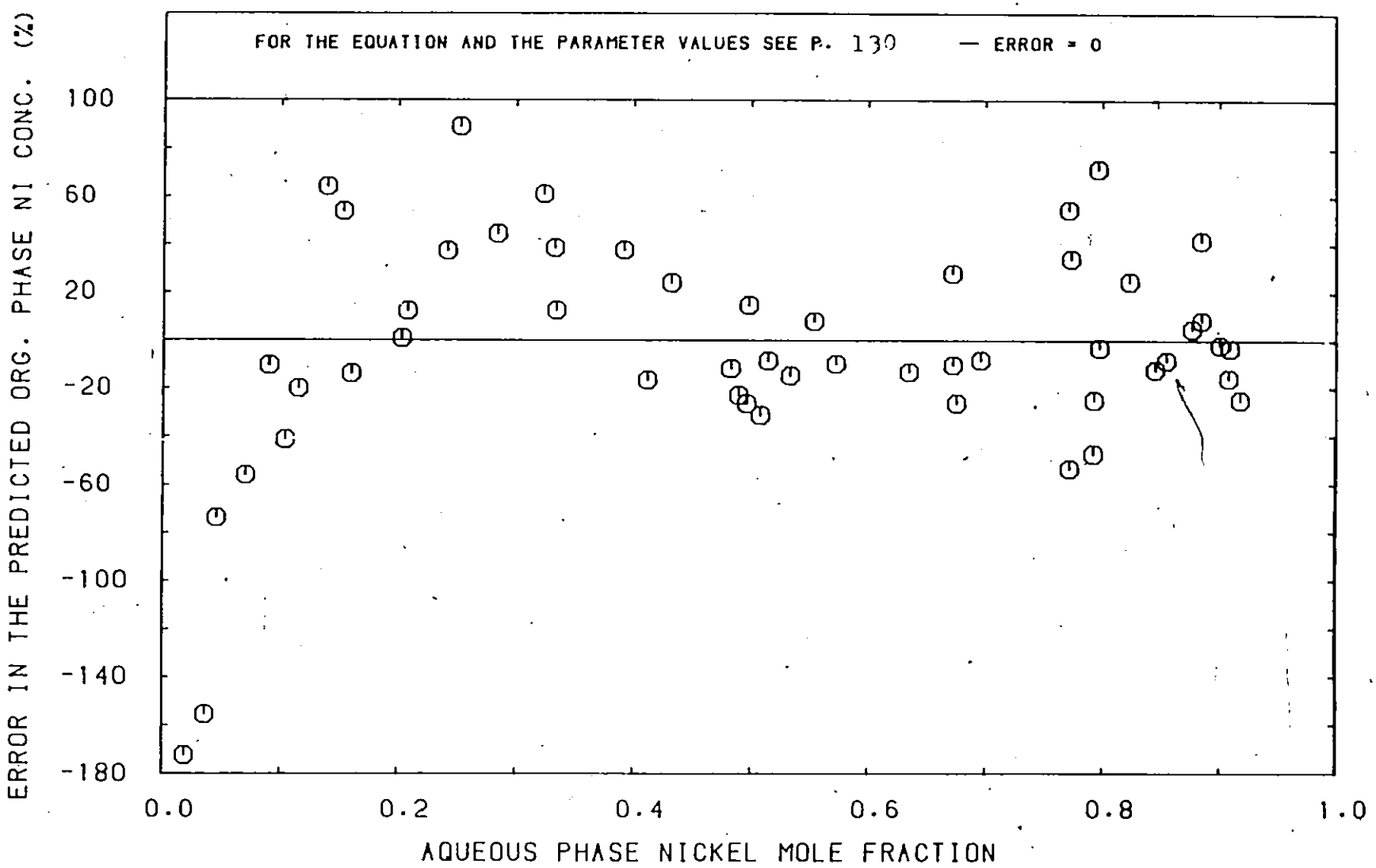


FIGURE 25A. ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE DELTA Y METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

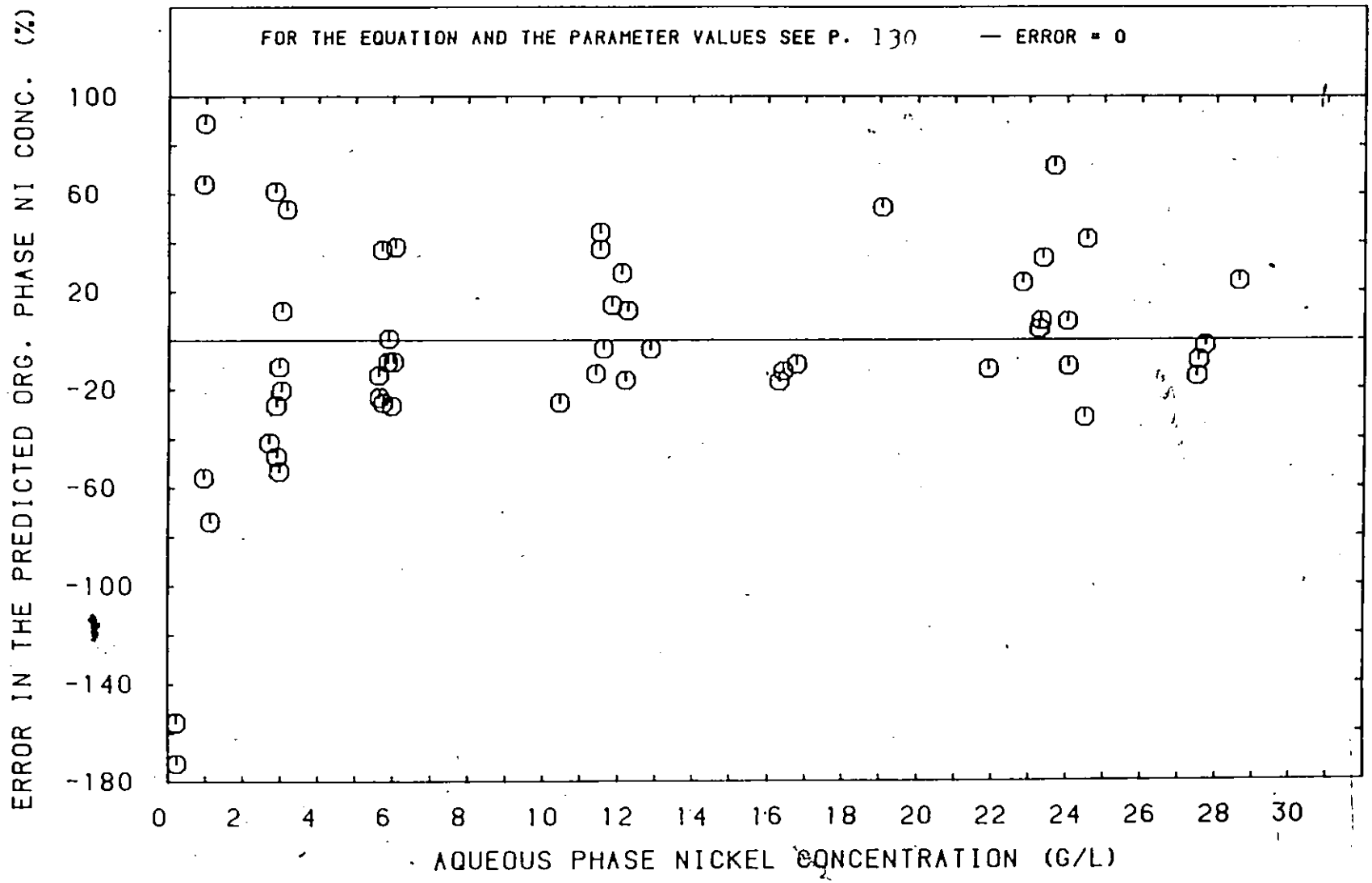


FIGURE 25B.ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE DELTA Y METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA. 75 % VARSOL DX3641. 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE; INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

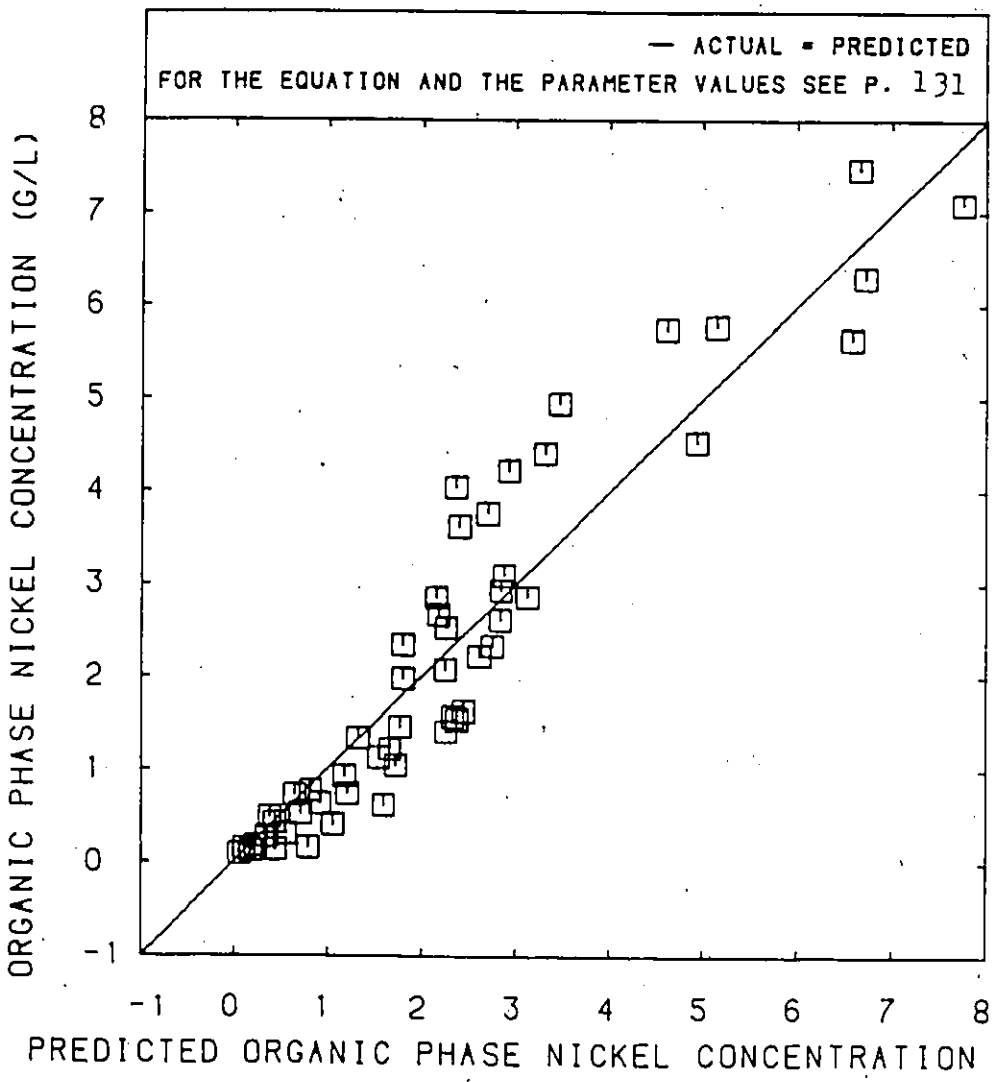


FIGURE 26. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE NICKEL CONCENTRATION FOR THE MOLE FRACTION METHOD AT 60 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4,
EQUILIBRIUM PH = 5.5-6.3; A/O = 1.

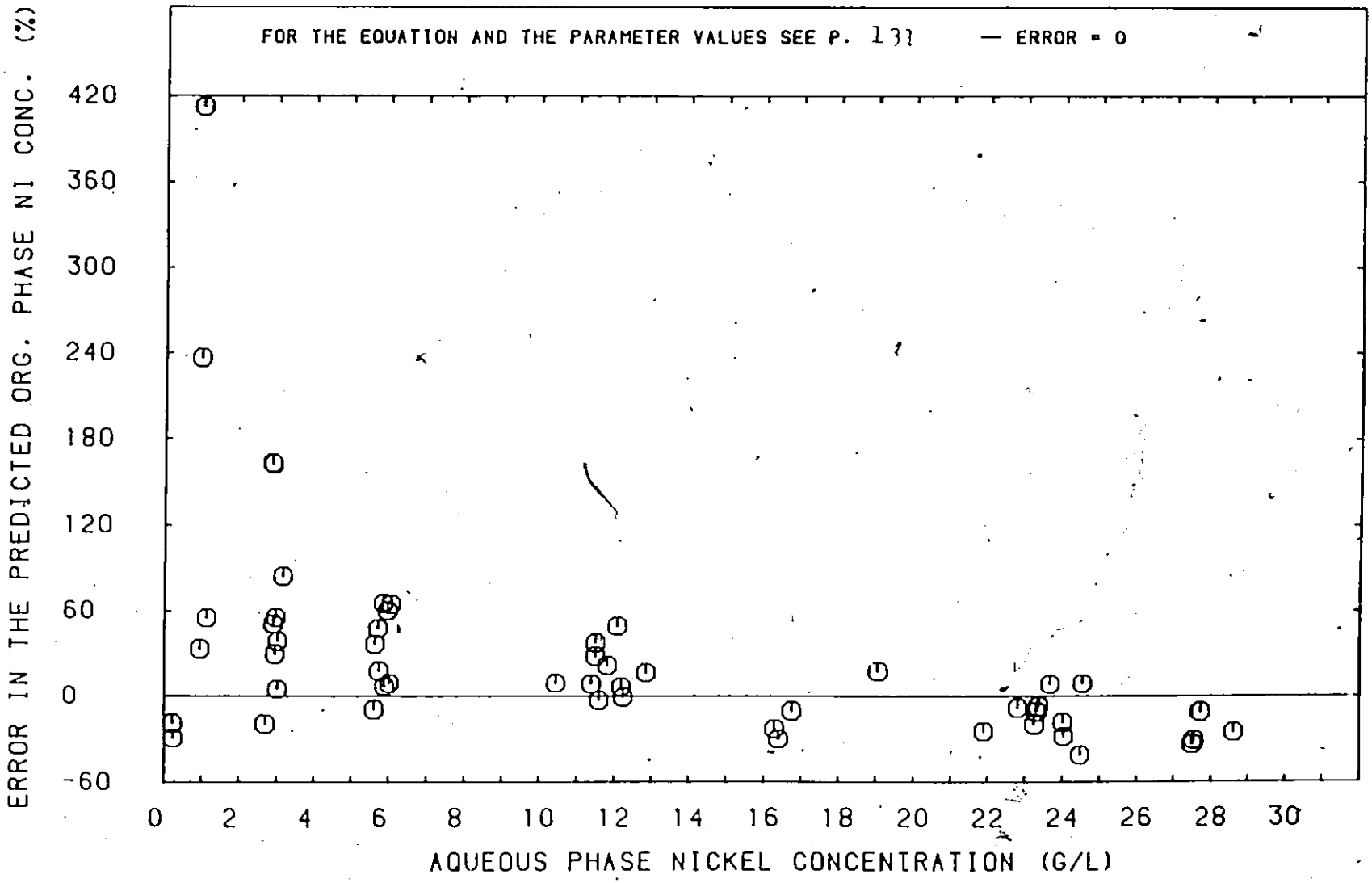


FIGURE 26A. ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE MOLE FRACTION METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

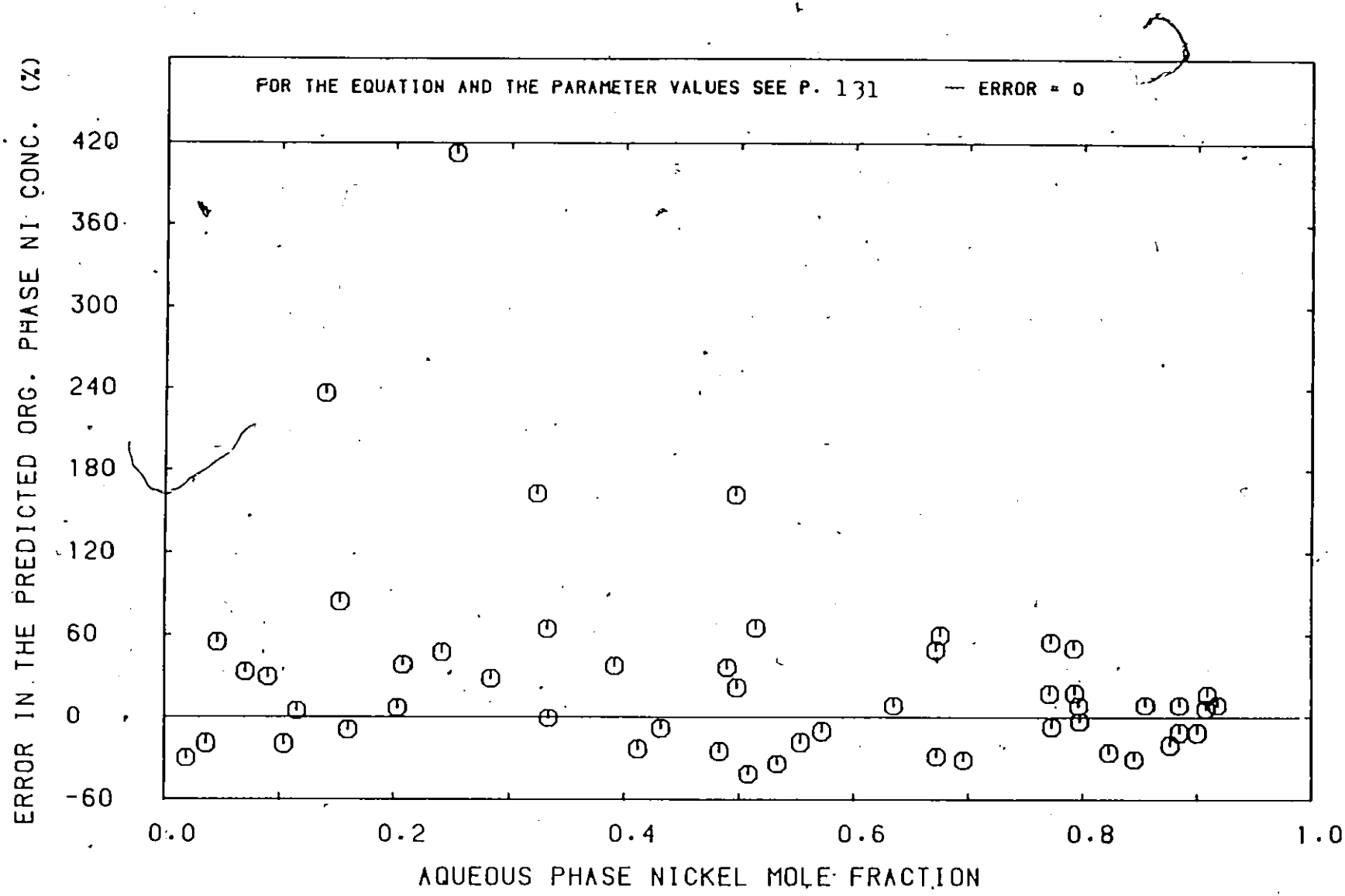


FIGURE 26B. ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE MOLE FRACTION METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

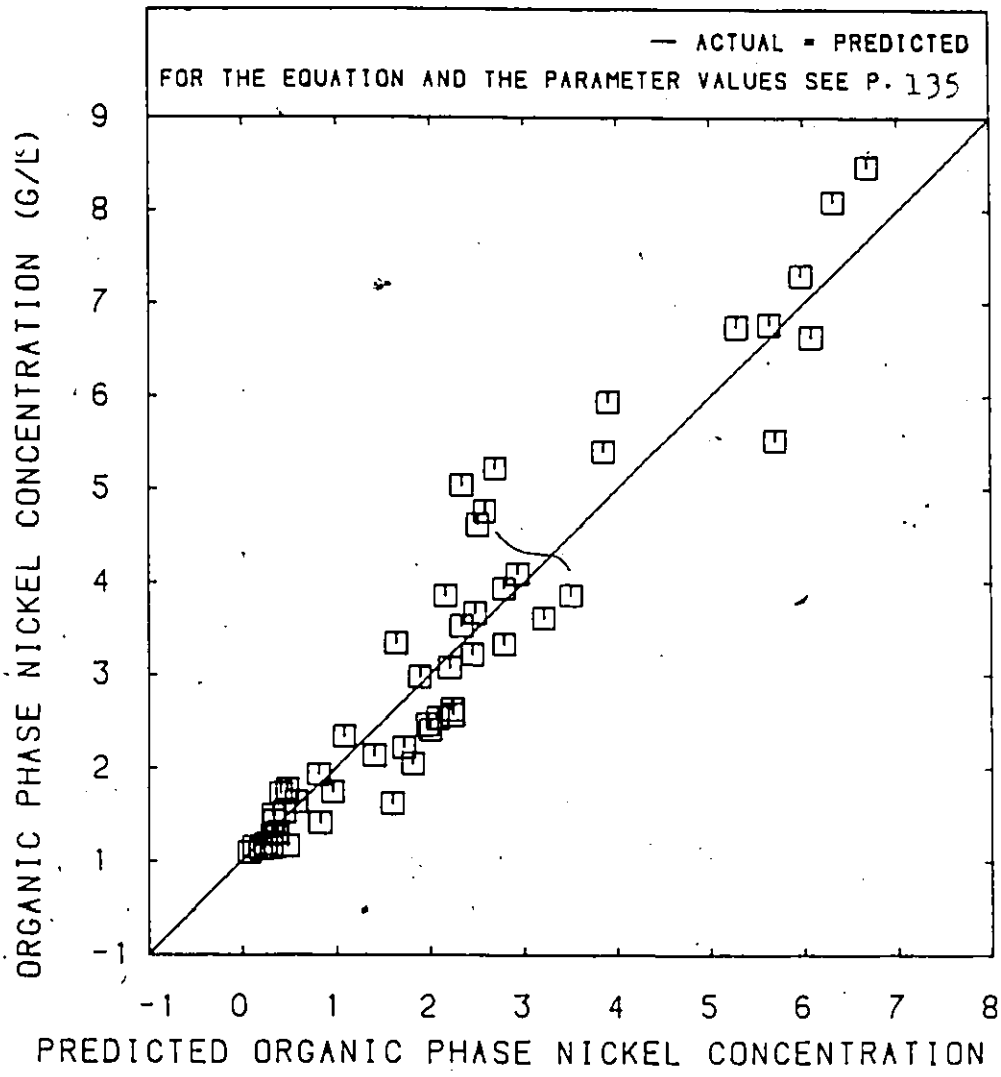


FIGURE 27. COMPARISON BETWEEN THE ACTUAL AND PREDICTED ORGANIC PHASE NICKEL CONCENTRATION FOR THE PSEUDO GAMMA METHOD AT 60 DEGREES CELSIUS

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP
AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4.
EQUILIBRIUM PH = 5.5-6.3; A/O = 1.

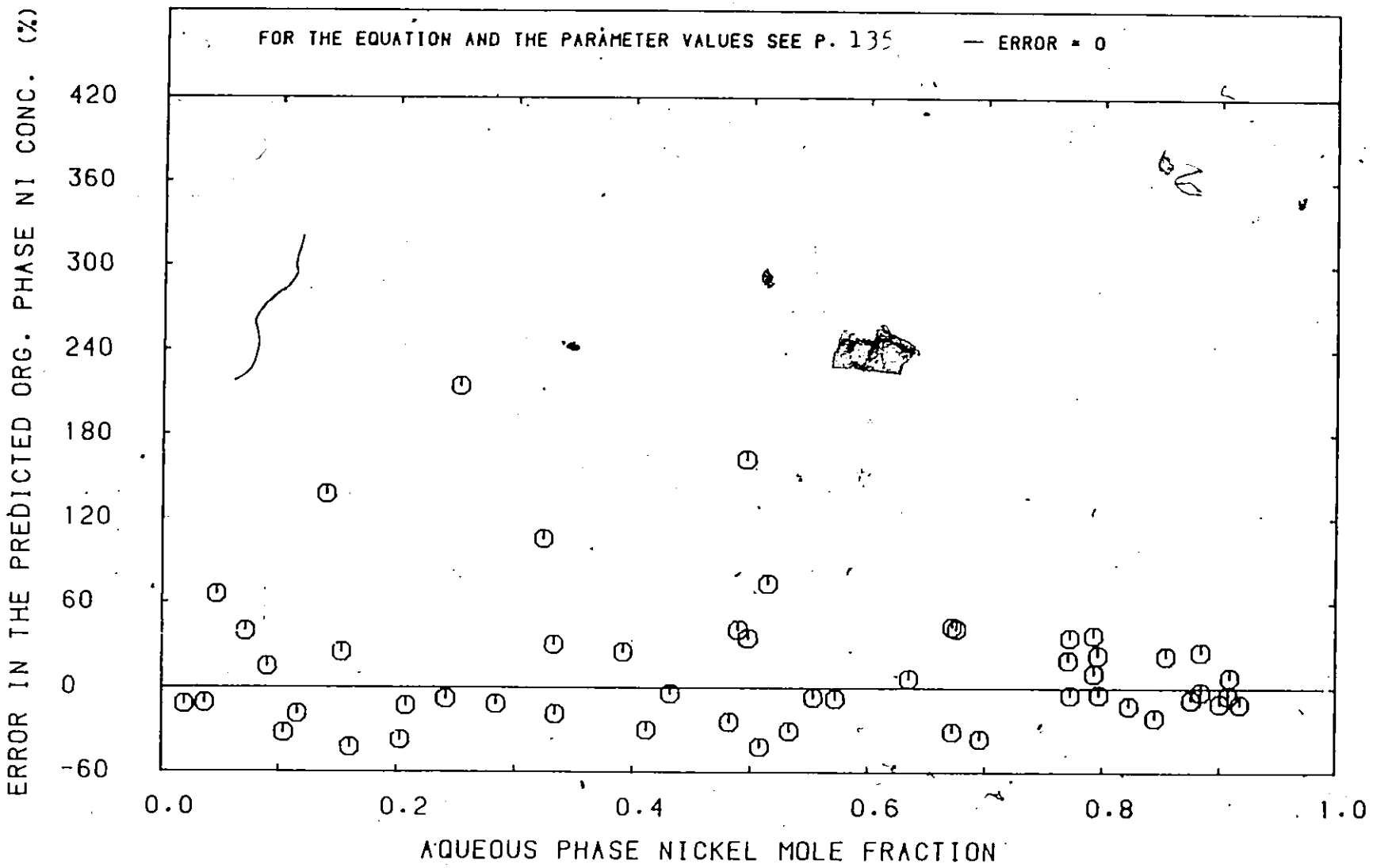


FIGURE 27A.ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE PSEUDO GAMMA METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE, INITIAL PH = 4, EQUILIBRIUM PH = 5.5-6.4.

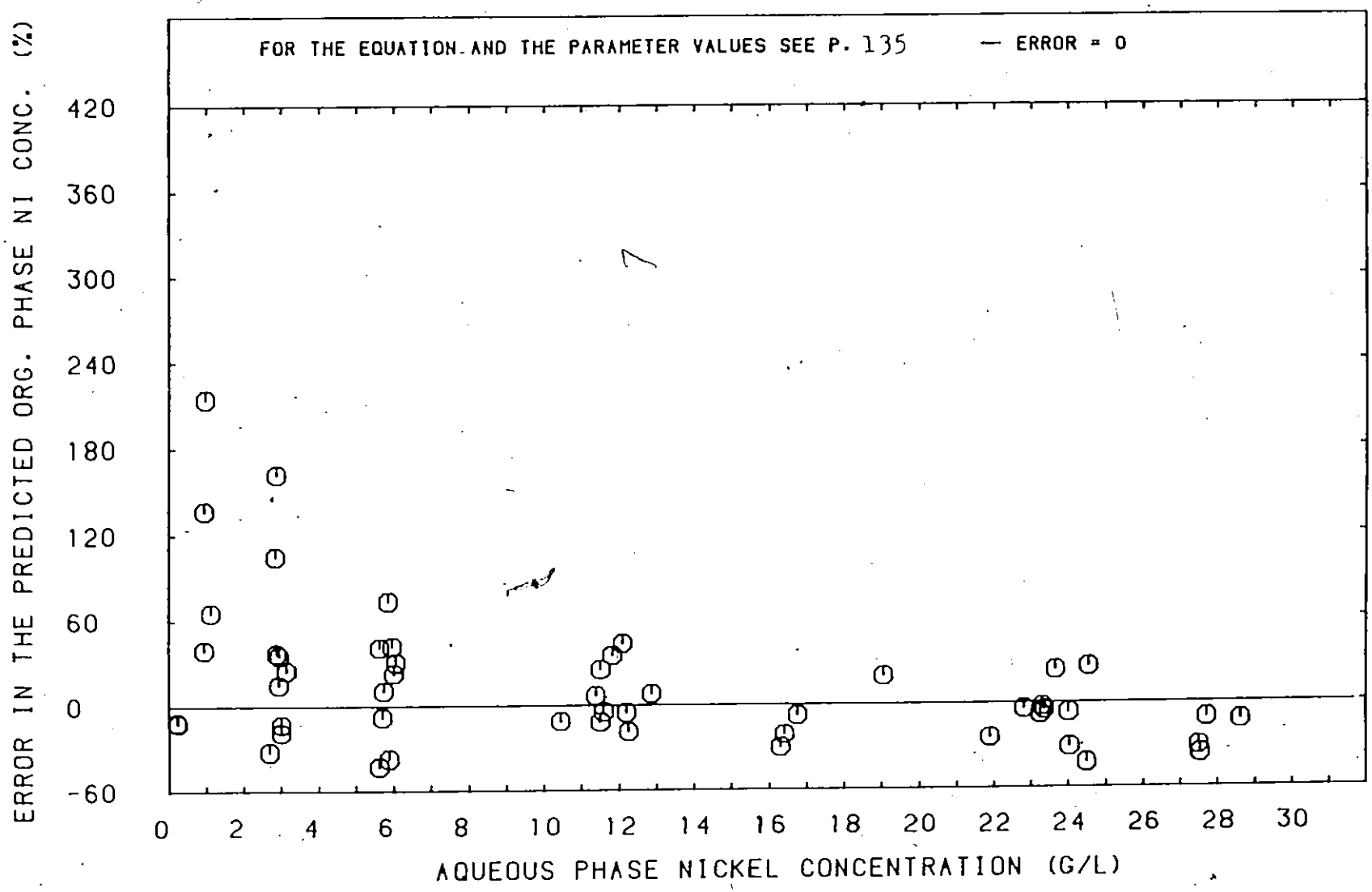


FIGURE 27B. ERROR IN THE PREDICTION OF THE ORGANIC PHASE NICKEL CONCENTRATION WITH THE PSEUDO GAMMA METHOD AT 60 DEG. C.

ORGANIC PHASE: 20 % D2EHPA, 75 % VARSOL DX3641, 5 % TBP; A/O = 1.

AQUEOUS PHASE: 20 G/L AMMONIUM SULPHATE. INITIAL PH = 4. EQUILIBRIUM PH = 5.5-6.4.

Appendix G

REAGENT SPECIFICATIONS

G.1 Nickelous Sulphate, 6-Hydrate

$NiSO_4 6H_2O$ FW = 262.9

Assay ($NiSO_4 6H_2O$) (by EDTA titration)	99.7 %
Insoluble matter	<0.001 %
pH of 5 % solution at 25 degrees Celsius	4.1
Chloride (Cl)	0.001 %
Nitrogen Compounds (as N)	<0.002 %
Substances not Precipitated by $(NH_4)_2SO_4$	0.08 %
Calcium (Ca) (by AAS)	0.0005 %
Cobalt and Manganese (as Co) (by AAS)	0.0003 %
Copper (Cu) (by AAS)	0.0001 %
Iron (Fe) (by AAS)	0.0006 %
Magnesium (Mg) (by AAS)	0.0003 %
Potassium (K) (by AAS)	0.0002 %
Sodium (Na) (bY AAS)	0.002 %
Trace Impurities (in ppm)	
Lithium (L) (by AAS)	1
Zinc (Zn) (by AAS)	1

G.2 Cobalt Sulphate, 7-Hydrate

$CoSO_4 7H_2O$ FW = 281.1

Assay ($CoSO_4 7H_2O$) (by EDTA titration)	98.4 %
Insoluble matter	<0.0003 %
pH of 5 % solution at 25 degrees Celsius	4.1
Chloride (Cl)	<0.001 %
Nitrate. (NO_3)	<0.001 %
Copper (Cu) (by AAS)	0.0004 %
Iron (Fe) (by AAS)	0.001 %
Lead (Pb) (by AAS)	0.001 %

Nickel (Ni), (by AAS)	0.04 %
Zinc (Zn) (bY AAS)	0.002 %

G.3 Ammonium Sulphate

$(NH_4)_2SO_4$ FW = 132.1

Assay $(NH_4)_2SO_2$ (by formol method)	99.8 %
Insoluble matter	0.001 %
Residue after ignition	0.004 %
pH of 5 % solution at 25 degrees Celsius	5.4
Nitrate (NO_3)	0.0003 %
Trace Impurities (in ppm)	
Chloride (Cl)	< 2
Phosphate (PO_4)	< 1
Arsenic (As)	< 0.2
Heavy Metals (as Pb)	< 2
Iron (Fe)	< 3

Appendix H

SOME PHYSICAL PROPERTIES OF EXPERIMENTAL REAGENTS

H.1 Solubilities

COMPOUND	TEMP. (°C)	SOLUBILITY (g/l)	REFERENCE
$NiSO_4 6H_2O$	0	625	(57)p.B-142
$CoSO_4 7H_2O$	3	604	(57)p.B-114
$(NH_4)_2SO_4$	0	706	(57)P.B-96
$(NH_4)_2SO_4 CoSO_4$	20	205	(57)p.B-95
$(NH_4)_2SO_4 NiSO_4$	20	104	(57)p.B-94

H.2 Miscellaneous Organic Compound Properties

H.2.1 D2EHPA

Molecular weight = 322.41 g/gmol
Density = 0.973 g/ml at 22 degrees Celsius (this work)

H.2.2 n-Tributyl Phosphate

Molecular weight = 266.32 g/gmol
Density = 0.9727 g/ml at 25 degrees Celsius (Ref 57 pp.C435)

H.2.3 VARSOL DX3641

Average Molecular Weight = 158 g/gmol (Note all values from Ref 19)
Density = 0.793 at 20 degrees Celsius
Flash point = 135 degrees Fahrenheit
Solubility parameter = 7.7
Viscosity = 1.165 cp at 25 degrees Celsius
Aromatic content = 6 wt %

Paraffinic content	= 45 wt %
Naphthenic content	= 49 wt %