THE SOLVENT EXTRACTION OF SOME METAL (II) PYRIDINE AND PICOLINE THIOCYANATES

by

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ABSTRACT

The pyridine and picoline thiocyanates of the metals cobalt, nickel, zinc and cadmium were studied, at 25.0°C, in equilibrated solvent-extraction systems.

The distribution ratio, D, defined as

$$D = \frac{\text{Total metal concentration in organic phase}}{\text{Total metal concentration in aqueous phase}}$$

was determined for each metal as a function of the equilibrium concentration of pyridine or picoline.

For an individual metal it was found that replacement of the pyridine molecule in the complex by a picoline resulted in a change in the distribution ratio for that metal with respect to other metals.

For each of the extracted metal pyridine and picoline thiocyanate complexes, the product of the partition coefficient and the overall formation constant in the aqueous phase was found.

The effects of temperature, pH, metal concentration, different solvents and steric hindrance were also studied.

A method of separating these metals by means of this solvent extraction system is suggested.

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LIST OF SYMBOLS

D = distribution ratio defined by $D = \dfrac{[A]_{T,o}}{[A]_{T,A}}$

where $[A]_{T,o}$ and $[A]_{T,A}$ are the total molar concentrations of A in the organic and aqueous phases, respectively.

E = percent extraction defined by

$$E = \frac{100\ D}{D + \frac{V}{V_o}}$$

where V and V_o are the equilibrium volumes of the aqueous and organic phases, respectively.

K_i = overall formation constant of the i^{th} complex.

k_i = stepwise formation constant of the i^{th} complex.

f_A = molar activity coefficient of A in aqueous solution.

$(f_A)_o$ = molar activity coefficient of A in non-aqueous solution.

(A) = thermodynamic activity of A in aqueous solution.

$(A)_o$ = thermodynamic activity of A in non-aqueous solution.

M = divalent transition metal.

P = pyridine or picoline.

Py = pyridine.

Pic = picoline.

PH^+ = pyridinium or picolinium ion.

PyH^+ = pyridinium ion.

$PicH^+$ = picolinium ion.

T = thiocyanate ion, or isothiocyanate ion.

$[A]$ = molar concentration of A, as A, in aqueous solution.

LIST OF SYMBOLS (continued)

$[A]_o$	=	molar concentration of A, as A, in non-aqueous solution.
p	=	partition coefficient.
g	=	gram.
mg	=	milligram.
μg	=	microgram.
l	=	liter.
ml	=	milliliter.
μl	=	microliter.
mμ	=	millimicron.
Å	=	Angstrom unit.
mv	=	millivolt.
ma	=	milliampere.
s_x	=	standard deviation calculated on the basis of N observations and N-1 degrees of freedom.

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PART I

GENERAL INTRODUCTION

1. Introduction

Solvent extraction may be defined as the distribution of any solute between two immiscible liquid phases. Its use is increasing, both in analytical chemistry and in some chemical and metallurgical industries. Morrison and Freiser (1) and Stary (24) have described the analytical uses. Marcus (2) recently presented a thorough general review of the field. Earlier basic papers by Irving and Williams (3) and by Irving, Rossotti and Williams (4) showed the need and the fruitfulness of a thermodynamic treatment of solvent extraction, and there have been applications of this rigorous treatment (24,25,75).

The present investigation comprised a study of the solvent extraction of the pyridine thiocyanates* and the picoline thiocyanates* of five divalent metals, from aqueous solutions into chloroform. The metals were cobalt, nickel, copper, zinc and cadmium. These metals were known to extract. Moreover, they are important industrial metals. Therefore, methods for their analytical or industrial separations from one another and from other metals may be of value. Thiocyanate was chosen because the relatively large size of this pseudo-halogen ion results in better extraction of the complexes into solvents of low-dielectric constant, than would occur with the smaller halogen ions.

Metal pyridine thiocyanates are well known. Some are relatively insoluble in water. Gravimetric determinations of manganese (29,85), iron (77), cobalt (6), nickel (7,86), copper (5,8,87,88,89,90,91,92), zinc (9,93,94) and cadmium (10) are based on this insolubility.

The solubility of some metal pyridine thiocyanates in chloroform and in other solvents has been exploited to provide useful analytical

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* For brevity, and in conformity with common usage, the term thiocyanate is used throughout for the complexes. However, the complexes studied were in fact isothiocyanates (96).

separations. For example, Forsythe, Magee and Wilson used solvent extraction to make several separations; nickel and cobalt were separated (14) by extraction of their pyridine thiocyanates into chloroform and hexone, respectively; palladium was separated from ruthenium (15), or from rhodium and platinum (102), by extraction of the pyridine thiocyanate into hexone.

The absorption spectra of the pyridine thiocyanates of cobalt, nickel and copper have been reported for the visible region (12). Moeller and Zogg (11) later reported in more detail the spectrum of copper pyridine thiocyanate. Ayres and Baird (13) used spectrophotometry for the simultaneous determination of manganese, iron, cobalt, nickel and copper as their pyridine thiocyanates. Very recently, Larson and Miezis (96) reported the infrared absorption spectra of the pyridine thiocyanates of cobalt, nickel, copper, zinc and cadmium.

Hunter and Miller (16) used anion exchange followed by solvent extraction into chloroform, for the separation of zinc, as the pyridine thiocyanate, from seventeen other elements.

King, Koros and Nelson (98) used infrared spectrophotometry to study the dissociation of cobalt pyridine and 2-picoline thiocyanates in chloroform. Graddon and Watton (100) have reported the magnetic properties, conductivities and absorption spectra in the visible region for cobalt 2-picoline and 4-picoline thiocyanates. The electronic spectra and magnetic moments of nickel pyridine, 3-picoline and 4-picoline thiocyanates have been reported by Nelson and Shepherd (97,99).

The solvent extraction of the metal picoline thiocyanates has not previously been reported.

It is evident then, that the metal pyridine thiocyanate system is an analytically useful one, particularly in solvent extraction; and indeed, methods for the separation and determination of some metals are now to be found in modern treatises (1,76).

However, previous investigators of this solvent-extraction system reported only the initial concentrations of reagents used in a particular phase; usually the initial concentration of pyridine in the aqueous phase. In any solvent-extraction study, values of the initial concentrations are not of general use, even though they may be sufficient for a particular procedure. Irving and Williams (3) emphasized the principle that equilibrium concentrations, not initial ones, should be reported in solvent-extraction studies. They stated that ".... the reason for rejecting most published data is they do not represent systems at equilibrium."

The reasons for preferring equilibrium conditions are evident: the Mass Law may be applied to sufficiently accurate and comprehensive data, to obtain partition coefficients and equilibrium constants; the data are of general validity, being independent of such variables as the volumes of phases; and solvent-extraction data on different metals in the same solvent-extraction system may legitimately be compared.

To report equilibrium concentrations for a solvent-extraction system requires much more experimental work than to report initial concentrations; not only must the analyses be carried out on the phases at equilibrium, but in many cases analytical methods must first be developed.

In order to plan the experimental work of the present investigation,

the physico-chemical basis of the solvent-extraction system was first considered; it is described in the following Section.

2. Physico-Chemical Basis of the Present Investigation

If an aqueous solution containing a metal ion and suitable ligands is equilibrated with an immiscible solvent, then the distribution ratio, D, of the metal is defined as follows:

$$D = \frac{\text{Total metal concentration in organic phase}}{\text{Total metal concentration in aqueous phase}} \qquad (1)$$

which may be abbreviated to

$$D = \frac{[M]_{T,o}}{[M]_{T,A}} \qquad (2)$$

where the subscripts T,o and T,A designate the total concentrations in the organic and aqueous phases, respectively. In the present discussion, $[A]$, f_A and (A) will represent the molar equilibrium concentration, molar activity coefficient* and activity, respectively, of the species A. The subscript o will designate the organic phase, and the absence of a subscript will designate the aqueous phase.

The following discussion will be specifically concerned with the distribution of divalent metal pyridine (or picoline) thiocyanates in equilibrated chloroform-water extraction systems.

For convenience, the following abbreviations will be used throughout for the participating substances:

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* The molar activity coefficient in the aqueous phase is designated by f_A; $(f_A)_o$ designates the molar activity coefficient in the organic phase.

M denotes divalent cobalt, nickel, copper, zinc or cadmium.

P denotes pyridine or a picoline.

T denotes the thiocyanate radical, SCN.

All monomeric metal pyridine (or picoline) thiocyanate species may then be abbreviated to MP_xT_2 (x is an integer) for divalent metals.

If an aqueous solution containing the divalent metal, pyridine (or picoline), and thiocyanate is equilibrated with an immiscible solvent of low dielectric constant, such as chloroform, then it will be supposed that the following complex species can exist in the organic phase: MP_xT_2 where x is an integer (x = 0 indicates MT_2), and dimers of MP_2T_2. Such dimers may be present in significant concentration, in low dielectric solvents such as chloroform or benzene, because this mixed complex would be expected to have a dipole moment. Ferguson (84) has shown, for example, that cobalt dipyridine thiocyanate (CoP_2T_2) dimerizes in chloroform solution. Higher aggregates of MP_2T_2 are not explicitly included in the following treatment; but the treatment would be mathematically similar to that used below for MP_2T_2. Ionization in a solvent of very low dielectric constant may safely be neglected.

The numerator (organic phase) of equation (2) may now be written as follows:

$$\text{Numerator} = \sum_{x=0}^{a} [MP_xT_2]_o + 2[M_2P_4T_4]_o \qquad (3)$$

The following equilibria may exist in the organic phase:

$$MT_2 + xP = MP_xT_2$$

and

$$K_x = \frac{(MP_xT_2)_o}{(MT_2)_o\,(P)_o^x} = \frac{[MP_xT_2]_o\,(f_{MP_xT_2})_o}{[MT_2]_o\,(f_{MT_2})_o\,[P]_o^x\,(f_P)_o^x} \qquad (4)$$

where K_x is the overall thermodynamic formation constant, and x is an integer.

For the formation of a dimer in the organic phase,

$$2MP_2T_2 = M_2P_4T_4 ,$$

and the dimerization constant, K_D, is given by

$$K_D = \frac{(M_2P_4T_4)_o}{(MP_2T_2)_o^2} = \frac{[M_2P_4T_4]_o\,(f_{M_2P_4T_4})_o}{[MP_2T_2]_o^2\,(f_{MP_2T_2})_o^2} \qquad (5)$$

Substitution of equations (4) and (5) into (3) gives

$$\text{Numerator} = \sum_{x=0}^{a} \frac{K_x[MT_2]_o\,(f_{MT_2})_o\,[P]_o^x\,(f_P)_o^x}{(f_{MP_xT_2})_o} \qquad (6)$$

$$+ \frac{2K_DK_2^2\,[MT_2]_o^2\,(f_{MT_2})_o^2\,[P]_o^4\,(f_P)_o^4}{(f_{M_2P_4T_4})_o}$$

The partition coefficient, p_o, for MT_2 is given by the following:

$$p_o = \frac{(MT_2)_o}{(MT_2)} = \frac{[MT_2]_o (f_{MT_2})_o}{[MT_2]\ f_{MT_2}} \tag{7}$$

Substitution of equation (7) into equation (6) gives

$$\text{Numerator} = p_o [MT_2] f_{MT_2} \left[\sum_{x=0}^{a} \frac{K_x [P]_o^x (f_P)_o^x}{(f_{MP_xT_2})_o} \right.$$

$$\left. + \frac{2K_D K_2^2 p_o [MT_2] f_{MT_2} [P]_o^4 (f_P)_o^4}{(f_{M_2P_4T_4})_o} \right] \tag{8}$$

For the denominator (aqueous phase) of equation (2), the following species were considered as possibly being present in the aqueous phase: MP_mT_n where m = 0, 1, 2, ... b and n = 0, 1, 2, ... c (MP_oT_o denotes M).

For simplicity, the charges on the ions have not been stated explicitly; they are implied throughout the present Section.

The denominator of equation (2) may then be represented as follows:

$$\text{Denominator} = \sum_{m=0}^{b} \sum_{n=0}^{c} [MP_mT_n] \tag{9}$$

The various equilibria in the aqueous phase are then represented

by the following

$$M + mP + nT = MP_mT_n$$

and

$$K_{mn} = \frac{(MP_mT_n)}{(M)(P)^m(T)^n} = \frac{[MP_mT_n]\, f_{MP_mT_n}}{[M]\, f_M [P]^m f_P{}^m [T]^n f_T{}^n} \qquad (10)$$

Substitution of equation (10) into equation (9) gives

$$\text{Denominator} = \sum_{m=0}^{b} \sum_{n=0}^{c} \frac{K_{mn}\, [M]\, f_M [P]^m f_P{}^m [T]^n f_T{}^n}{f_{MP_mT_n}} \qquad (11)$$

Since

$$K_{02} = \frac{(MT_2)}{(M)(T)^2} = \frac{[MT_2]\, f_{MT_2}}{[M]\, f_M [T]^2 f_T{}^2}$$

then

$$[MT_2]\, f_{MT_2} = K_{02}\, [M]\, f_M [T]^2 f_T{}^2 \qquad (12)$$

Substitution of equations (8), (11) and (12) into equation (2) gives

$$D = \frac{p_o K_{02} \left[\sum_{x=0}^{a} \frac{K_x [P]_o^x (f_P)_o^x}{(f_{MP_xT_2})_o} + \frac{2K_D K_2^2\, p_o\, K_{02} [M]\, f_M [T]^2 f_T{}^2 [P]_o^4 (f_P)_o^4}{(f_{M_2P_4T_4})_o} \right]}{\sum_{m=0}^{b} \sum_{n=0}^{c} \frac{K_{mn} [P]^m f_P{}^m [T]^{n-2} f_T{}^{n-2}}{f_{MP_mT_n}}} \qquad (13)$$

which is the sought-for general expression for the distribution ratio of a metal in the specified solvent-extraction system.

If dimers do not exist in the organic phase, then $K_D = 0$ and equation (13) reduces to

$$D = \frac{p_o K_{02} \sum_{x=0}^{a} \frac{K_x [P]_o^x (f_P)_o^x}{(f_{MP_xT_2})_o}}{\sum_{m=0}^{b} \sum_{n=0}^{c} \frac{K_{mn} [P]^m f_P^m [T]^{n-2} f_T^{n-2}}{f_{MP_mT_n}}} \qquad (14)$$

From equations (13) and (14) the following useful observations may be made, provided that activity coefficients are constant for the solutions investigated, and that dimers are absent:

(1)

$$\left(\frac{\partial D}{\partial (M)} \right)_{(P),(T)} = 0 \qquad (15)$$

This relationship constitutes a test for the existence of dimers.

(2) At constant $[P]$, D is a function only of $[T]$. Thus

$$D = \frac{1}{\sum_{n=0}^{c} C_n [T]^{n-2}} \qquad (16)$$

where C_n is a series of constants.

(3) At constant $[T]$, D is a function only of $[P]$, since $(P)_o$ and (P) are related by a partition coefficient. Thus

$$D = \frac{\sum_{x=0}^{a} C_x [P]_o^x}{\sum_{m=0}^{b} C'_m [P]^m} \qquad (17)$$

where C_x and C'_m are two series of constants.

The percent extraction, E, of the metal is related to its distribution ratio, D, by the relationship

$$E = \frac{100\ D}{D + V/V_o} \qquad (18)$$

where V and V_o designate the equilibrium volumes of the aqueous phase and the organic phase, respectively. Therefore if the distribution ratio and the phase volumes are known, the percent extraction may be calculated.

From equation (17) it is seen that

$$\lim_{[P]\to 0} D = \frac{C_o}{C'_o} \qquad (19)$$

and D will have a minimum value which is unique for each metal.

An example of how D and E may vary with the equilibrium pyridine (or picoline) concentration [P] is shown in Figs. 1A and 1B, respectively.

Equation (17) may also be written as follows:

$$D = \frac{\sum_{x=0}^{4} C_x [P]_o^x}{\sum_{m=0}^{6} C'_m [P]^m}$$

FIGURE 1

The effect of the equilibrium concentration of pyridine (or picoline) on the distribution ratio of the metal (Figs. 1A and 1C) and the resultant effect on the percent extraction of the metal (Figs. 1B and 1D, respectively).

DISTRIBUTION RATIO OF METAL.
PERCENT EXTRACTION OF METAL.
100
60
20
1 A.
1 B.
1 C.
1 D.
EQUIL. MOLARITY OF PYRIDINE.
EQUIL. MOLARITY OF PYRIDINE.

The summation in the numerator of equation (20) is over four integers since (a) a maximum coordination number of six is found with divalent transition metals and (b) complexes in a low-dielectric organic phase will be electrically neutral. Since the latter restriction does not apply to complexes in the aqueous phase then metal penta- and hexapyridine ions may exist in the aqueous phase*. It is then evident that the rate of increase in the numerical value of the denominator may be greater, over a range of pyridine (or picoline) concentrations, than that rate of increase in the numerator of equation (20). Should this circumstance arise in practice, then the distribution ratio will decrease; this implies that the distribution ratio can have a maximum value. An example of how D and E may vary, under these circumstances, with the pyridine or picoline concentration, $[P]$, is shown in Figs. 1C and 1D respectively.

Guided by equations (13) to (17), experiments were devised to elucidate the chemistry of the specified solvent-extraction systems. The full scope of the investigation is described in the next Section.

3. The Present Investigation

The investigation consisted essentially of an experimental study of the distribution, at equilibrium, of metal pyridine and picoline thiocyanates between an aqueous phase and chloroform.

It was necessary first to develop the analytical methods needed to determine the equilibrium concentrations of the various participating species. This development included the determination of the accuracy and precision of the methods.

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* There is conclusive spectral evidence (124) for the existence of nickel penta- and hexapyridine ions.

For this solvent-extraction system, the distribution ratio, D, of the metal is seen from equation (13) to be a function of the equilibrium concentrations of thiocyanate, $[T]$, pyridine or picoline, $[P]$ and, in the case where polynuclear species exist, of the metal, $[M]$. For the present study, a special case of equation (13) was applied. It is represented by equation (17), for which the equilibrium concentration of thiocyanate ions in the aqueous phase is constant. This case had the advantage that the ionic strength of the solution was almost constant, so that the activity coefficients of the various ionic species in the aqueous solution were likely to be nearly constant. Moreover, the proportions of the various ionic thiocyanate complexes of the metal would be essentially constant in the absence of polynuclear species.

Equation (17) indicates that D, and therefore E (the percent metal extracted), are fairly complicated functions of the equilibrium concentration of pyridine (or picoline). Nevertheless, a plot of E versus $[P]$, the equilibrium concentration of pyridine (or picoline) should give a sigmoid curve similar to that shown in Fig. 1B, or in Fig. 1D. However, the position of this curve along the axis for the pyridine or picoline concentration will be unique for each metal, since this position depends on the various equilibrium constants and partition coefficients for the complexes of that metal. The present experimental investigation was directed specifically toward obtaining the equilibrium data necessary in order to be able to plot these sigmoid curves.

By inspection of these sigmoid curves, it would be possible to determine the feasibility of analytical (or industrial) separations amongst the various metals, the optimum range of concentrations of pyridine or

picoline to be used, and the degree of completeness of the separation. Such curves, then, represent the most potentially useful form of analytical information about this solvent-extraction system.

The use of the picolines introduced new and interesting factors. The inductive effect of the alkyl substituent and its steric hindrance were expected to result in partition coefficients and equilibrium constants different from those for pyridine. Consequently, potentially useful horizontal shifts in the positions of the various sigmoid curves were expected when picolines were substituted for pyridine.

The concentration of metal was varied in some experiments, in order to determine whether or not polynuclear species of the metal could be detected. From equation (15) it is evident that the distribution ratio of the metal should be independent of metal activity, only in the absence of polynuclear species.

Finally, it was proposed to make the best possible use of the experimental data, namely the sigmoid curves, in order to obtain estimates of the formation constants of the metal pyridine and picoline thiocyanates that were present in the chloroform phase.

PART II

MATERIALS

1. Glassware

All volumetric glassware was calibrated both for aqueous and non-aqueous solutions. For example, a pipette that delivered 10.00 ml of water at 25°C was found to deliver 9.95 ml of chloroform. This 0.5 percent decrease was found to be constant for other 10-ml pipettes, and for various 25-ml and 50-ml pipettes calibrated under similar conditions. Burettes were found to deliver equal volumes* of either chloroform or water. Volumetric flasks were found to contain the same volumes* of either chloroform or water. Temperature corrections were made on measured volumes where necessary.

Only borosilicate glassware was used. Before each use, it was thoroughly cleaned, then rinsed first with tap water, then with distilled water, and finally with conductivity water (see below). Glassware to be used with non-aqueous solutions was finally air-dried before use.

2. Reagents

All the reagents used were of analytical reagent grade (Analar or A.C.S. specifications), and except as noted below, they were used without further purification.

Aqueous solutions were prepared with conductivity water (see below).

Some aqueous solutions may be affected by adsorption or desorption processes with the container. Therefore, all standard and stock solutions of the chlorides of cobalt, nickel, copper, zinc and cadmium,

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* To within a volumetric tolerance of one part per thousand.

ethylenediaminetetraacetic acid, sodium chloride, calcium chloride and sodium hydroxide were stored in polyethylene bottles.

The organic components of the non-aqueous solutions were found to diffuse into polyethylene. Therefore, these solutions were stored in glass containers.

Light-sensitive solutions or reagents were stored either in the dark or in brown bottles. For example, the reagents chloroform, pyridine and the picolines as well as Nitroso-R salt solutions were stored in the dark, and solutions of potassium thiocyanate and silver nitrate were stored in brown bottles.

Pyridine, the picolines, chloroform and water were specially purified by methods described in detail in Appendix I. Notes on these methods and on the products follow.

2-1. Conductivity Water

Distilled water was passed through a column of mixed-bed ion-exchange resin in accordance with the directions given in Appendix I-1. The product had a specific resistance of 2.2×10^5 ohms. Kirk and Othmer (78) have pointed out that "a good grade of specially prepared distilled water" has a specific resistance of this magnitude.

In order to test for the presence of metal ions in concentrations significant for the present investigation, 100 ± 10 ml of the conductivity water were titrated with a 0.01-M solution of ethylenediaminetetraacetic acid (EDTA) by using Murexide as the indicator. Less than 0.02 ml of EDTA was required to complete the titration, which showed that

less than 0.2 micromole of total titratable cation was present.

The absence of any turbidity even 12 hours after the addition of silver nitrate to the acidified conductivity water showed that the chloride content must have been less than 10^{-5}M.

Therefore, it was concluded that the purity of the conductivity water was adequate for the purposes of the present investigation.

2-2. Carbon Dioxide-Free, Anhydrous Chloroform

The fractional distillation procedure recorded in Appendix I-3 was used to remove carbon dioxide from chloroform; the product also was presumed to be anhydrous. The method is similar to that used by Pearson and Vogelsong (18) for the preparation of pure anhydrous chloroform. However, the purpose of the present purification was not to prepare an anhydrous product, but to remove carbon dioxide. When the final product was shaken with an aqueous solution of barium hydroxide, there was no precipitate of barium carbonate. This fact, together with the fact that carbon dioxide is readily boiled out of water, was taken as sufficient evidence for the absence of carbon dioxide from the purified chloroform.

Ethanol, normally present in reagent-grade chloroform as a preservative, was then added to the purified chloroform, since the fractional distillation had removed it (79).

2-3. Pyridine, 2-Picoline, 3-Picoline and 4-Picoline

These reagents were purified by fractional distillation, as

described in Appendix I-5. The method is similar to that described by Brown and Mihm (22) for the purification of these reagents for the determination of their pK_a values in water. Through cooling-curve studies, Brown and Cahn (95) found that the picolines obtained by using the above fractional distillation procedure had purities that were "greater than 99 percent". In the present investigation, the dehydrating agent was anhydrous barium oxide (BaO) as suggested by Leis and Curran (20), instead of calcium hydride (22).

Each of the purified reagents was clear and colorless. The boiling points were: pyridine, 115.0°C (115.0°C); 2-picoline, 129.0°C (129.0°C); 3-picoline, 143.5°C (144.0°C); 4-picoline, 144.5°C (145.0°C); literature values (21) are in brackets. Each of these boiling points was measured during the fraction distillation with a thermometer (50-150°C, 0.5°C divisions) which, in the present work, was previously calibrated against a standard 100-200°C thermometer obtained from the National Research Laboratories. The atmospheric pressure at the time of each temperature measurement was not recorded. Therefore, the recorded temperatures were not corrected for any variation of the prevailing atmospheric pressure from one atmosphere.

The purified pyridine and the picolines were analysed for impurities by gas chromatography. A gas-chromatographic method was developed in order to determine pyridine or 2-picoline in the presence of one another and in the presence of 3-picoline and 4-picoline. The details of this method are in Appendix II. Both pyridine and 2-picoline had elution peaks separate from one another and from either 3-picoline or 4-picoline (see Fig. 2).

FIGURE 2

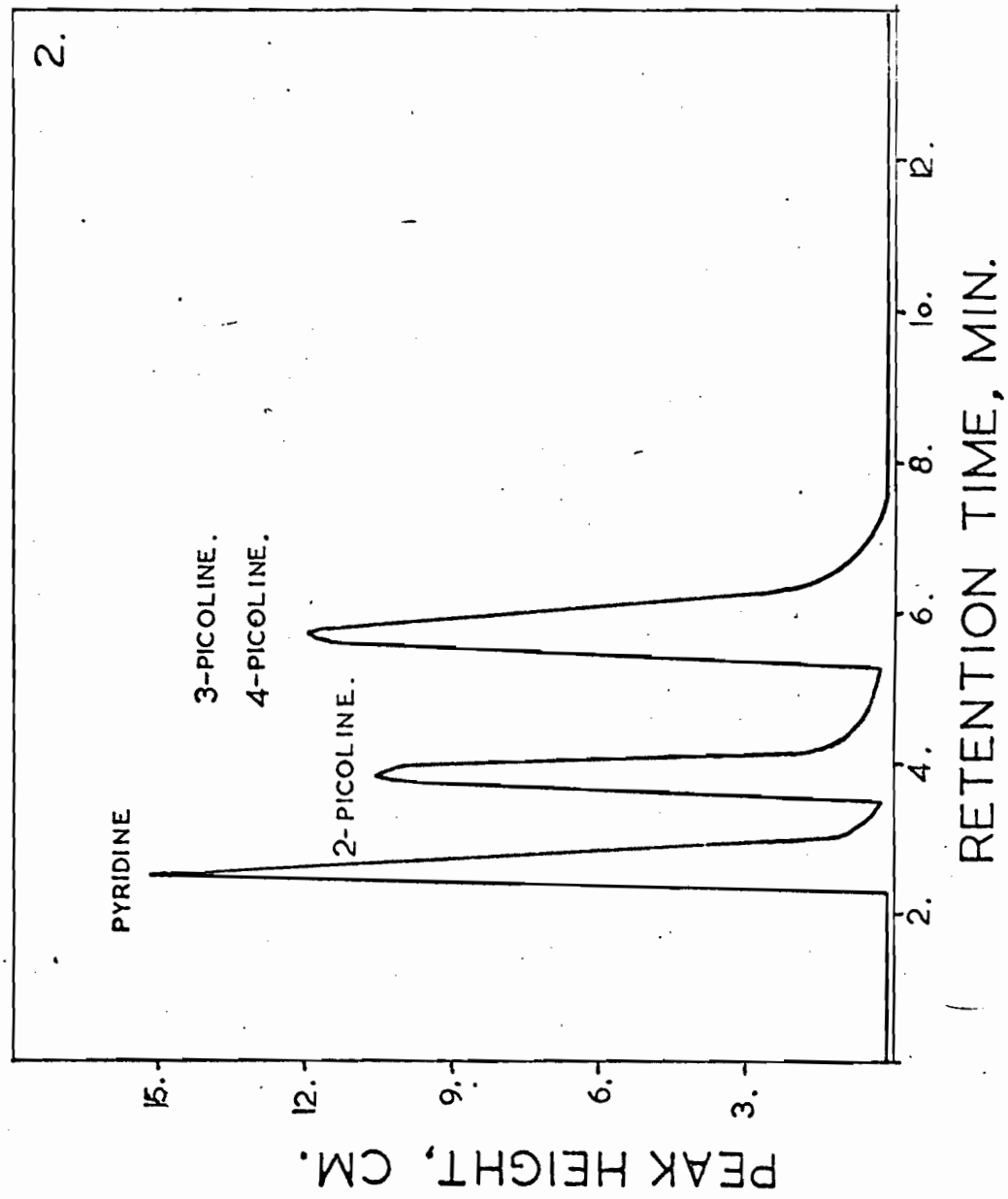
Gas chromatogram of a sample containing equal volumes of purified pyridine, purified 2-picoline, purified 3-picoline and purified 4-picoline.

Column description: 6-foot column (1/4" O.D.) of Apiezon L on Fisher "Columpak".

Operating temperature: 70°C.

Sample size: 4 µl.

(For full experimental details, see Appendix II).


2.
PYRIDINE
2-PICOLINE.
3-PICOLINE.
4-PICOLINE.
15.
12.
9.
6.
3.
PEAK HEIGHT, CM.
2.
4.
6.
8.
10.
12.
RETENTION TIME, MIN.

It was found that the purified pyridine contained less than 0.1 percent of the picolines; the purified 2-picoline contained less than 0.1 per cent of both pyridine and the other picolines; and the purified 3-picoline and 4-picoline contained less than 0.1 per cent of both pyridine and 2-picoline.

However, 3-picoline and 4-picoline had nearly identical elution times under the chosen operating conditions. Therefore, another method was developed in order to determine 3-picoline in 4-picoline and vice versa.

Nuclear magnetic resonance* was tried in order to determine these two isomers in the presence of one another. However, the resonance peaks were coincident when either chloroform, benzene, carbon tetrachloride or no carrier solvent was used.

A gas-chromatographic method, described in Appendix III, was then developed. Standard solutions of 4-picoline in 3-picoline and of 3-picoline in 4-picoline were prepared with the purified reagents. Their gas chromatograms are shown in Figs. 3 and 4, respectively. The chromatogram of the major constituent was drawn freehand underneath the impurity shoulder. Then the line which encircled the area corresponding to the impurity was traced onto heavy cardboard; the tracing was cut out and then weighed. In Fig. 5, the measured weights are plotted against the percent of added picoline impurity in the standard solutions. This method is the well-known method of addition, where a reagent, containing an unknown concentration of a given impurity, is "salted" with known amounts of that impurity. By extrapolation of the graph to zero

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* A Varian HR-60 was used.

FIGURE 3

Gas chromatograms of samples of purified 3-picoline containing different added amounts of purified 4-picoline.

Column description: 6-foot column (1/4" O.D.) of tris 1,2,3(2-cyano ethoxy)propane on Fisher "Chromosorb W".

Operating temperature: 98°C.

Sample size: 0.9 µl.

(For full experimental details, see Appendix III).

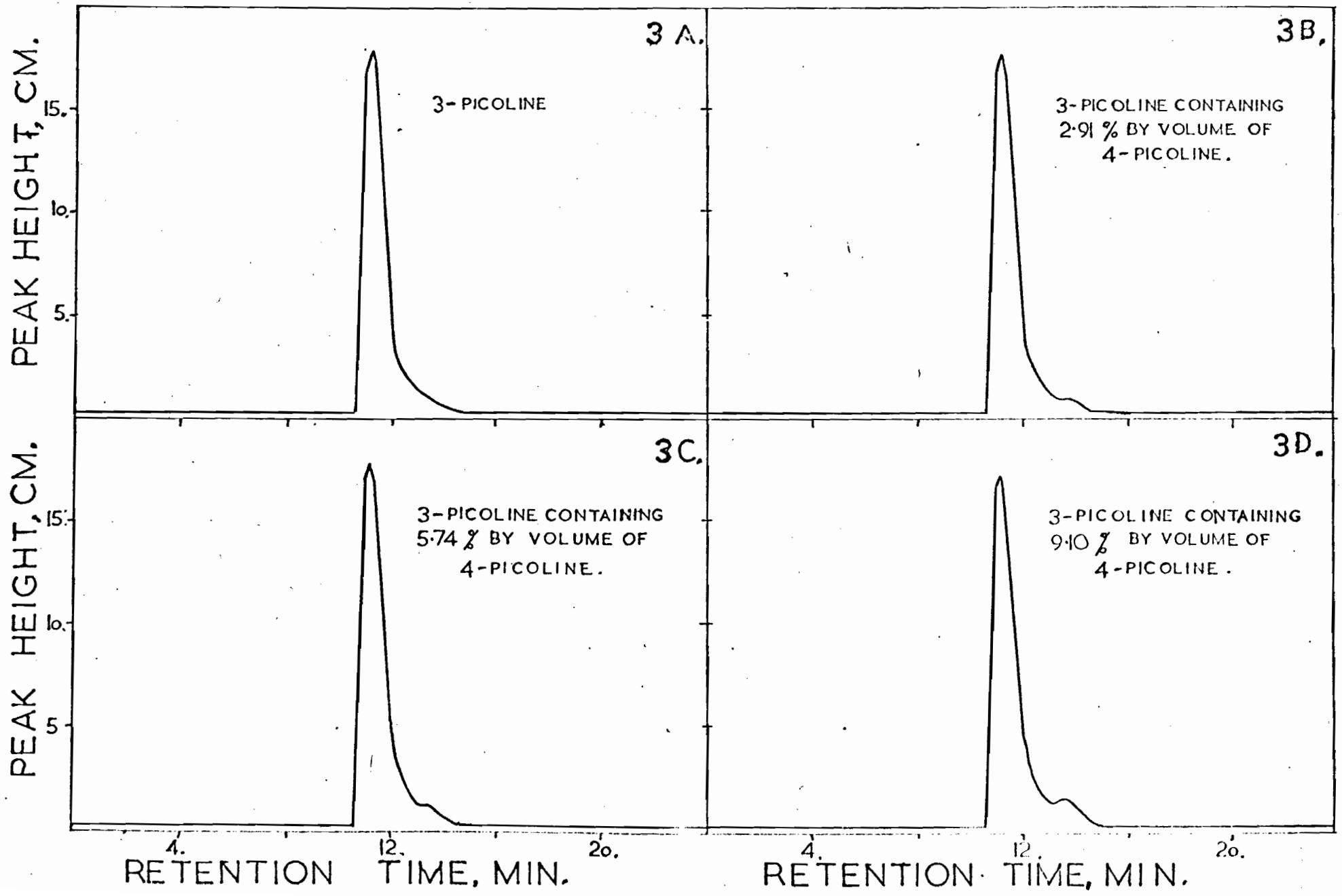

3 A.
3-PICOLINE
3B.
3-PICOLINE CONTAINING
2·91 % BY VOLUME OF
4-PICOLINE.
3C.
3-PICOLINE CONTAINING
5·74 % BY VOLUME OF
4-PICOLINE.
3D.
3-PICOLINE CONTAINING
9·10 % BY VOLUME OF
4-PICOLINE.
PEAK HEIGHT, CM.
15.
10.
5.
PEAK HEIGHT, CM.
15.
10.
5
4.
12.
20.
RETENTION TIME, MIN.
4.
12.
20.
RETENTION TIME, MIN.

FIGURE 4

Gas chromatograms of samples of purified 4-picoline containing different added amounts of purified 3-picoline.

Column description: 6-foot column (1/4" O.D.) of tris 1,2,3(2-cyano ethoxy)propane on Fisher "Chromosorb W".

Operating temperature: 98°C.

Sample size: 0.9µl.

(For full experimental details, see Appendix III).

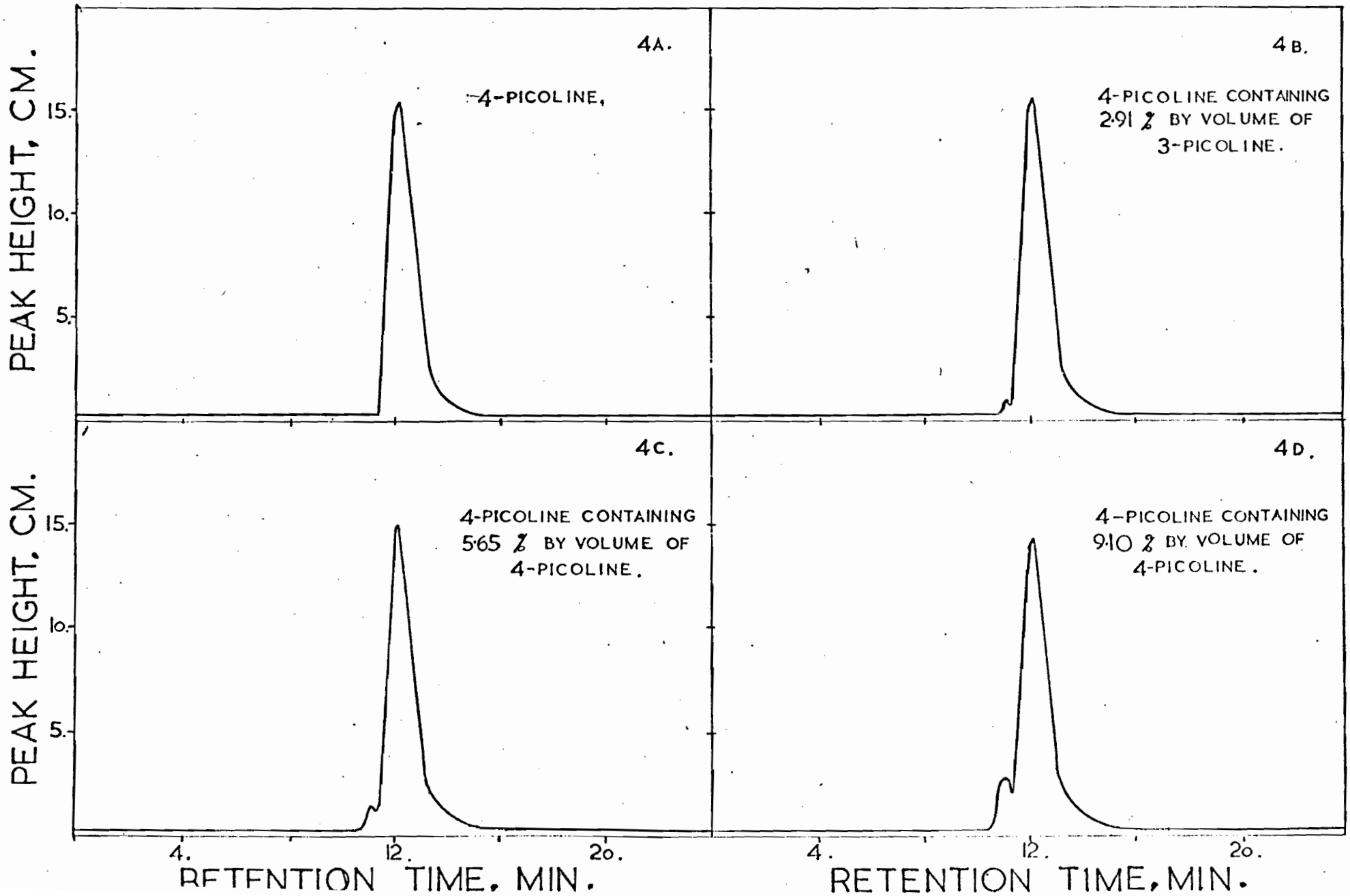
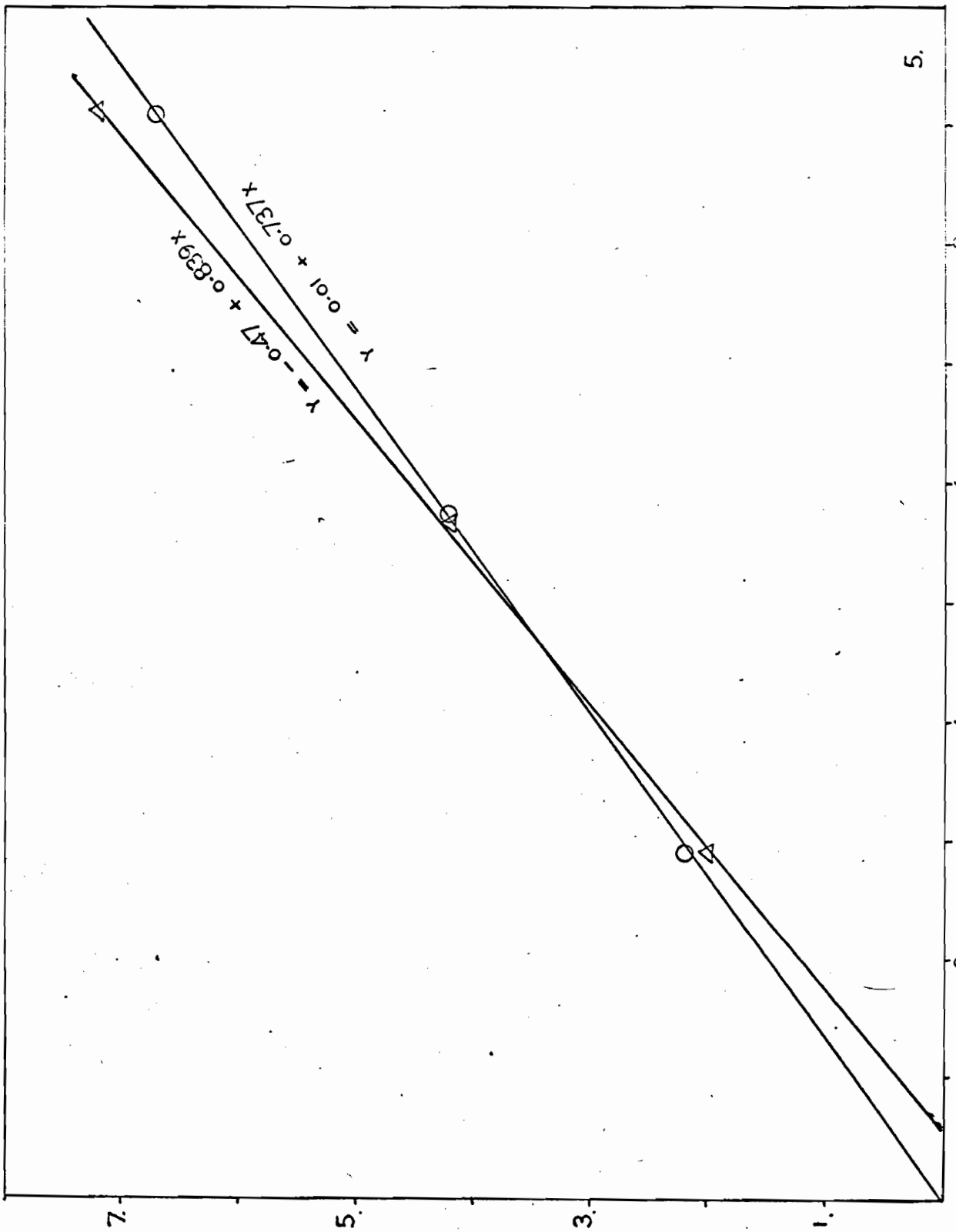

4A.
4-PICOLINE.
4B.
4-PICOLINE CONTAINING
2·91 % BY VOLUME OF
3-PICOLINE.
4C.
4-PICOLINE CONTAINING
5·65 % BY VOLUME OF
4-PICOLINE.
4D.
4-PICOLINE CONTAINING
9·10 % BY VOLUME OF
4-PICOLINE.
PEAK HEIGHT, CM.
15.
10.
5.
4.
12.
20.
RETENTION TIME, MIN.

FIGURE 5

Area under chromatogram peak due to added impurity, versus percent of impurity added; the least squares line (101) for each set of data is noted.

△ = 3-picoline impurity in 4-picoline.

⊙ = 4-picoline impurity in 3-picoline.


AREA UNDER IMPURITY PEAK, ARBITRARY UNITS.
PICOLINE IMPURITY, PERCENT BY VOL.
y = 0.01 + 0.737x
y = -0.47 + 0.839x

5.

concentration of added impurity, it is possible to read the amount of the impurity present in the "unsalted" sample. Extrapolation of the lines* in Fig. 5 indicated that the purified 4-picoline contained 0.56 percent of the 3-picoline, and that the purified 3-picoline was free from 4-picoline.

The behavior of the 3-picolinates and the 4-picolinates in the solvent-extraction system will be shown later to be almost identical. Therefore the 0.56 percent isomeric impurity in the 4-picoline was not important.

Finally, the purified pyridine and the purified picolines were assayed by potentiometric titration of weighed samples against a standard solution of perchloric acid in dioxane. The procedure is in Appendix VIII. These assays gave: pyridine, 99.9 percent; 2-picoline, 99.9 percent; 3-picoline, 99.7 percent; 4-picoline, 99.5 percent. That each of these assays represents almost entirely the parent compound is evident from the gas chromatographic analyses.

Therefore, it was concluded that the purity of the purified pyridine and of each purified picoline was adequate for the purposes of the present investigation.

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* The lines which best fitted the data were determined by the method of least squares (101). The equations of these lines are given in Fig. 5.

PART III

EXTRACTION PROCEDURE

In order to obtain quantitative results, it was first necessary to develop a suitable extraction procedure. It was also necessary to correct for any volume changes on extraction. A simple method was devised, which provided the necessary volume corrections, without requiring the quantitative separation of the two immiscible phases.

The detailed procedures are in the Appendices, but their development is described below.

1. The Extraction Procedure

Preliminary experiments had shown that the solvent-extraction systems were very temperature-dependent; this study is described in Part V-3. Therefore, during all stages of a solvent extraction, the system was kept in a water thermostat. The extraction vessel immersed in the bath was mechanically* shaken in order to achieve equilibrium.

A 500-ml conical flask of borosilicate glass** was used as the extraction vessel; a separatory funnel proved too unwieldy to clamp in the shaker. An indentation was blown in the side of the flask in order to permit the clamp of the mechanical shaker to hold it. The flask had a bakelite screw cap. A Teflon insert was used in this cap, because the usual plastic insert was attacked by chloroform. In order to ensure a watertight seal between this insert and the rim of the flask, the rim was ground flat by using first a carborundum disc and then a

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* A Burrell "Wrist-Action" shaker was used.

** Extraction vessels of polyethylene were also tried, but they were discarded because pyridine and chloroform were found to diffuse into the wall.

fine diamond sandpaper.

The manipulative details of the extraction procedure are given in Appendix IV.

2. Volume Changes in Extraction Systems

Herz (23) stated that at 22°C, 100 ml of water dissolved 0.42 ml of chloroform, and 100 ml of chloroform dissolved 0.15 ml of water. These mutual solubility values were found (80,81) to change by less than 6 percent between 20°C and 30°C.

Pyridine and the picolines have distribution ratios favoring chloroform (see Part V-4-1). In addition, chloroform normally contains 0.95 percent of ethanol as a preservative. Apparently its distribution ratio between chloroform and water has not been reported.

These facts made it advisable to determine the equilibrium volumes of the two phases in the extraction systems used in the present investigation. This determination involved the use of an aqueous solution and a chloroform solution, the composition and volumes of which were known. The two solutions were equilibrated* at room temperature, then the two phases were separated and their volumes measured. These volumes were corrected for the mechanical losses in volume in a solvent-extraction operation, to give the true equilibrium volumes. The details of this method are in Appendix V.

Table I shows the results. The presence of thiocyanate in the aqueous phase had no significant effect on the final phase volumes

* Although it was not proved here that equilibrium had been established, equilibrium was known to be attained very rapidly in systems of this kind (see Part V-3 for a complete study). Therefore it was assumed that equilibrium was also established in the extraction systems described here.

TABLE I

Initial versus final (equilibrium) phase volumes of chloroform - water extraction systems containing pyridine and thiocyanate

Extraction temperature : Room temperature.
Procedure : See Appendix V.

Expt. No.	Description of phases before extraction		Final (equilibrium) phase volumes,* ml			
	Aqueous	Chloroform	Aqueous	S_x	Chloroform	S_x
1	100 ml water	100 ml chloroform	101.3	0.1	98.8	0.2
2	100 ml water containing 810 mg pyridine	"	100.5	0.1	99.7	0.1
3	100 ml water containing 270 mg pyridine	"	101.0	0.1	99.0	0.2
4	100 ml 0.1-M potassium thiocyanate containing 810 mg pyridine	"	100.5	0.1	99.6	0.2
5	100 ml water	100 ml chloroform containing 810 mg pyridine	101.3	0.1	98.7	0.2

* Means of 5 replicates.

(Expts. 2 and 4). The data from experiments 1, 2 and 3, plotted in Fig. 6, showed the useful fact that the final phase volumes were a linear function of the initial pyridine concentration in the aqueous phase.

Table II was then constructed by assuming that (i) all the alcohol present in the chloroform phase was extracted into the aqueous phase; (ii) 100 ml of chloroform dissolved 0.15 ml of water; (iii) 100 ml of water dissolved 0.42 ml of chloroform; (iv) the distribution ratio of pyridine between chloroform and water was 15. This table gives the contributions that each distributed species would then be expected to make towards the change in the initial volume of a phase, due to equilibration of the two phases.

The experimental final phase volumes of Table I were then compared with the values expected on the basis of Table II. The results are in Table III. They support the above assumptions. Therefore, the final (equilibrium) phase volumes may be calculated if the initial pyridine concentration of one phase is known.

The general extraction procedure (Appendix IV) used throughout the present investigation utilized initial volumes of 90 ml. In addition, the extra manipulation in that procedure was found to result in an evaporation loss of 1.1 percent* of the chloroform. By including these factors with the volume data reported above, Table IV was constructed. It gives the corrected volumes for the solvent-extraction systems treated by the general procedure in Appendix IV.

Corrected volumes were similarly computed for systems that

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* Mean of 4 replicates; S_x = 0.1 percent.

FIGURE 6

Phase volumes, at room temperature, of chloroform-water extraction systems containing pyridine.

NOTE: Data are from Table I.

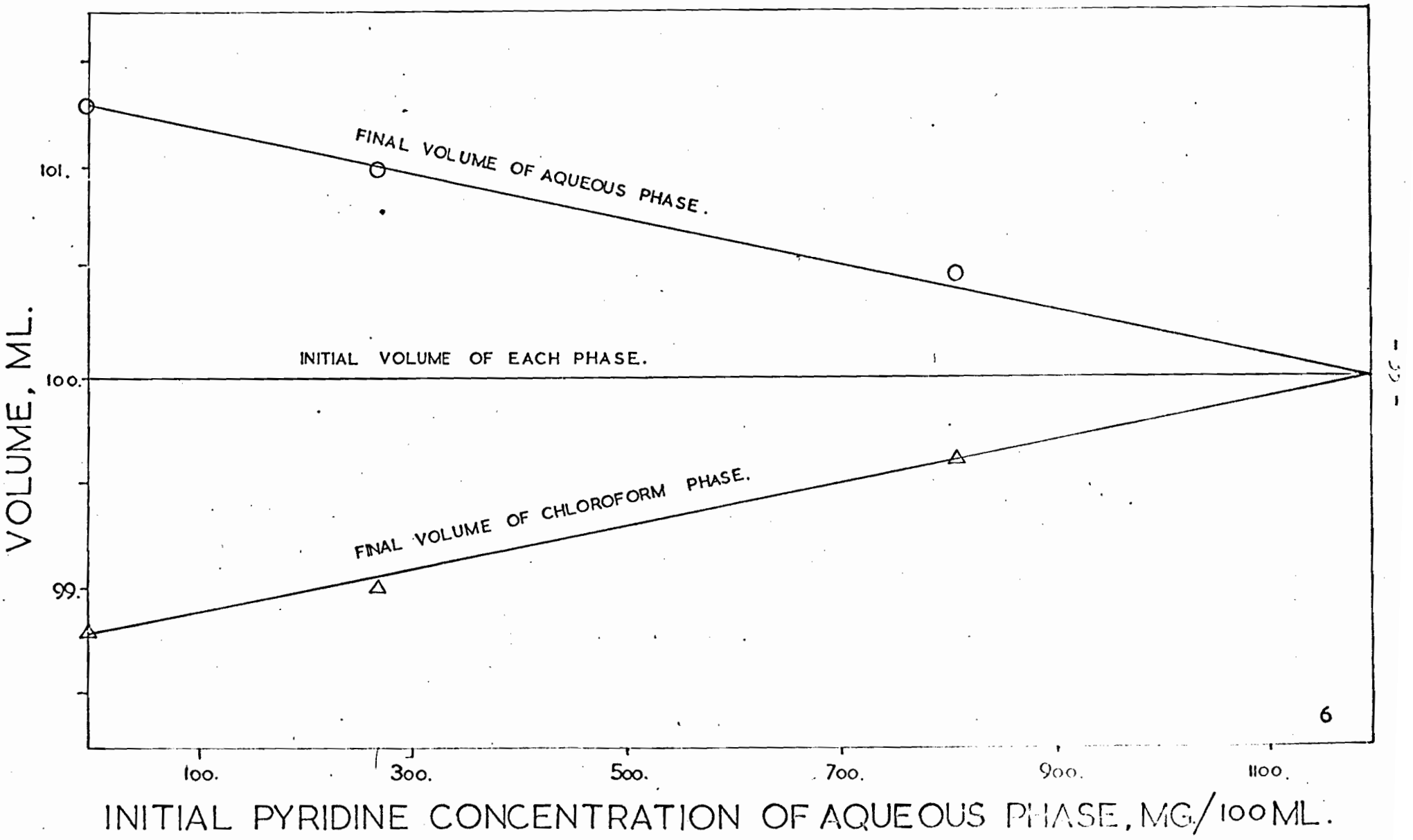
FINAL VOLUME OF AQUEOUS PHASE.
INITIAL VOLUME OF EACH PHASE.
FINAL VOLUME OF CHLOROFORM PHASE.
VOLUME, ML.
101.
100.
99.
100.
300.
500.
700.
900.
1100.
INITIAL PYRIDINE CONCENTRATION OF AQUEOUS PHASE, MG./100 ML.
6

TABLE II

Contributions of distributed species to the change in initial volume of a phase, due to equilibration

Initial volume of each phase : 100 ml.

Contribution No.	Source of contribution	Contribution (ml) applied to 100 ml of phase	
		Aqueous	Chloroform
1	Solubility of water in chloroform	-0.15	+0.15
2	Solubility of chloroform in water	+0.42	-0.42
3	Extraction of alcohol from chloroform into water	+0.95	-0.95
4	Distribution of 810 mg of pyridine initially present in aqueous phase	-0.78	+0.78
5	Distribution of 270 mg of pyridine initially present in aqueous phase	-0.26	+0.26
6	Distribution of 810 mg of pyridine initially present in chloroform phase	+0.04	-0.04

NOTE: Density of pyridine taken to be 0.98 (21).

TABLE III

Comparison of calculated and measured volumes of equilibrium phases in the water - chloroform - pyridine systems

Initial volume of each phase : 100 ml.

Expt. No.	Contribution numbers applied (see Table II)	Final (equilibrium) phase volumes, ml			
		Expected		Measured*	
		H_2O	$CHCl_3$	H_2O	$CHCl_3$
1	1, 2, 3	101.2	98.8	101.3	98.8
2	1, 2, 3, 4	100.5	99.5	100.5	99.7
3	1, 2, 3, 5	101.0	99.0	101.0	99.0
4	1, 2, 3, 4	100.5	99.5	100.5	99.6
5	1, 2, 3, 6	101.3	98.7	101.3	98.7

* Data are from Table I.

TABLE IV

Final (equilibrium) phase volumes for chloroform - water extraction systems containing pyridine, 3-picoline or 4-picoline

Initial volume of each phase : 90 ml.
Extraction temperature : 25.0°C.

Pyridine or picoline taken, mg (in H_2O)	Final (equilibrium) phase volume, ml			
	Pyridine		3-Picoline or 4-Picoline	
	H_2O	$CHCl_3$	H_2O	$CHCl_3$
0-50	91.2	87.8	91.2	87.8
51-150	91.1	87.9	91.1	87.9
151-250	91.0	88.0	91.0	88.0
251-350	90.9	88.1	90.9	88.1
351-450	90.8	88.2	90.8	88.2
451-550	90.7	88.3	90.6	88.4
551-650	90.6	88.4	90.5	88.5
651-750	90.5	88.5	90.4	88.6
751-850	90.4	88.6	90.3	88.7
851-950	90.3	88.7	90.2	88.8
951-1050	90.2	88.8	90.1	88.9
1051-1150	90.1	88.9	90.0	89.0
1151-1250	90.0	89.0	89.9	89.1
1251-1350	89.9	89.1	89.8	89.2
1351-1450	89.8	89.2	89.7	89.3
1451-1550	89.7	89.3	89.6	89.4

NOTES : (1) Where alcohol-free chloroform was used, subtract 0.8 ml from the aqueous volume and add 0.8 ml to the chloroform volume.
(2) The presence of pyridinium or picolinium chloride did not affect the phase volumes.
(3) The presence of potassium thiocyanate did not affect the phase volumes.

(Continued)

TABLE IV (continued)

Final (equilibrium) phase volumes for chloroform - water extraction system containing 2-picoline

Initial volume of each phase : 90 ml.
Extraction temperature : 25.0°C.

2-Picoline taken, mg (in H_2O)	Final (equilibrium) phase volume, ml	
	H_2O	$CHCl_3$
0-50	91.2	87.8
1351-1450	89.8	89.2
3251-3350	87.9	91.1
4451-4550	86.8	92.2
6851-6950	84.1	94.9
8951-9050	82.0	97.0
11451-11550	79.4	99.6
13451-13550	77.4	101.6
16051-16150	74.7	104.3
17951-18050	72.7	106.3
22451-22550	68.2	110.8
33251-33350	57.1	121.9
47451-47550	42.4	136.6

NOTES : (1) Where alcohol-free chloroform was used, subtract 0.8 ml from the aqueous volume and add 0.8 ml to the chloroform volume.
(2) The presence of potassium thiocyanate did not affect the phase volumes.

contained a picoline instead of pyridine. Each picoline has a density of about 0.95 (21) and a distribution ratio that also favors chloroform (see Part V-4-1). These corrected volumes are also in Table IV.

PART IV

DEVELOPMENT OF THE ANALYTICAL METHODS

The development of analytical methods was a necessary prerequisite to solvent-extraction studies of metal pyridine (and picoline) thiocyanates. The final methods are prescribed in Appendices; their development is described below.

1. Pyridine or Picoline in Aqueous Solutions

A method was necessary for the determination of the pyridine (or picoline) content of the equilibrated aqueous phase of the metal pyridine (or picoline) thiocyanate extraction systems.

The direct spectrophotometric determination of pyridine or picolines was not possible. Although pyridine and the picolines have characteristic absorption peaks in the ultraviolet region (22), the 0.3-M thiocyanate employed also absorbed strongly below 280 mμ. Moreover, pyridinium or picolinium ions were added to some systems. Their peaks overlap those of pyridine.

Polarography was also investigated. Knobloch (26) reported that pyridine could be determined in this way, but he did not state the accuracy and precision of the method. In the present investigation, a similar method was tested. It was found not to be sufficiently precise. For example, 5×10^{-4}-M pyridine was determined with a standard deviation of 4×10^{-5} M (based on 4 replicates).

The titration of pyridine with standard hydrochloric acid has been reported by Kolthoff and Stenger (27). They detected the end point by using a mixed indicator, methyl yellow-methylene blue. In the present investigation, pyridine concentrations down to about 5×10^{-4}M were expected. At this low level, the indicator gave an indistinct end point.

Moreover some of the solutions would be colored.

Therefore, a conventional potentiometric method was adopted, by titrating the base against standard hydrochloric acid, and using a glass-calomel pair of electrodes. The procedure is in Appendix VI. This procedure was also expected to be satisfactory for the picolines, since they are slightly stronger bases than is pyridine (22).

The accuracy and precision of the method were estimated. Thus, standard aqueous solutions of purified pyridine and of the purified picolines were prepared by weight. Aliquots of the solutions were diluted volumetrically. Replicate samples from these solutions were titrated against standard hydrochloric acid. The results are in Table V. Typical titration curves for pyridine are shown in Fig. 7; the titration curves for the picolines were similar. In practice, the end points for all pyridine and picoline titrations were found algebraically by the conventional method of second differences (49).

It was necessary also to determine pyridine (or picoline) in the presence of pyridinium (or picolinium) chloride*. This determination was also carried out by the procedure given in Appendix VI. The accuracy and precision of this determination were estimated as follows: standard solutions were prepared; each solution contained a measured amount of standard hydrochloric acid, and a measured amount of purified pyridine.

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* This salt was added to some systems in order to reduce the pH of the aqueous phase. It was found that pyridinium and picolinium chloride were not extracted as such into chloroform. Therefore a method was not required for the determination of pyridinium (or picolinium) ion in the presence of pyridine (or picoline). However, a satisfactory method is given in Appendix X, for completeness.

TABLE V

Accuracy and precision of the potentiometric determination of pyridine and the picolines in aqueous solutions

Sample size : 25 ml.
Titrant : Standard aqueous solution of hydrochloric acid.
Procedure : See Appendix VI.

Test solution	No. of replicates	Titrant molarity	Increments of titrant near end point, ml	Pyridine or Picoline, mg		
				Taken	Found*	Sx
0.1 M Pyridine	5	0.1	0.5	184.5	184.5	0.5
0.01 M "	5	0.1	0.1	18.45	18.26	0.15
0.001 M "	5	0.025	0.1	1.84	1.81	0.02
0.0005 M "	5	"	0.1	0.85	0.83	0.01
0.001 M 2-Picoline	4	"	0.05	2.53	2.50	0.03
0.001 M 3-Picoline	4	"	0.05	2.41	2.39	0.03
0.001 M 4-Picoline	4	"	0.05	2.33	2.32	0.02

* Means of replicates.

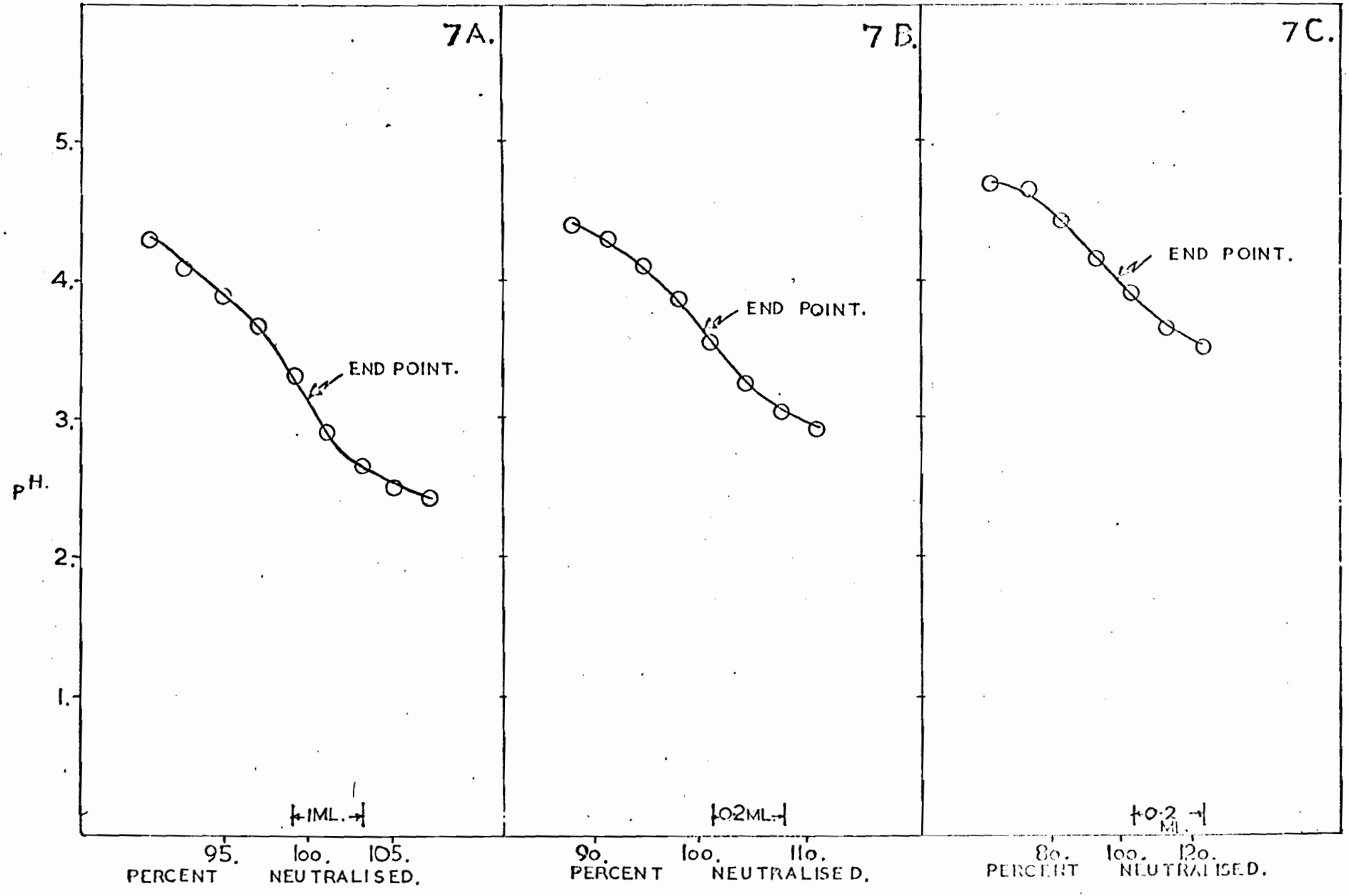
FIGURE 7

Typical potentiometric titration curves for the determination of pyridine in aqueous solutions.

(A) 0.1-M pyridine vs 0.1-M hydrochloric acid.

(B) 0.01-M pyridine vs 0.1-M hydrochloric acid.

(C) 0.001-M pyridine vs 0.025-M hydrochloric acid.


7A.
7B.
7C.
5.
4.
3.
2.
1.
pH.
END POINT.
END POINT.
END POINT.
1ML.
·2ML.
·2 ML.
95.
100.
105.
PERCENT NEUTRALISED.
90.
100.
110.
PERCENT NEUTRALISED.
80.
100.
120.
PERCENT NEUTRALISED.

Aliquots of each solution were then titrated potentiometrically for pyridine. Other aliquots were titrated separately for pyridinium chloride, by using the procedure given in Appendix X*. The results are in Table VI. In all titrations reported, the acid end points were determined by the conventional method of second differences (49).

It remained to be shown that pyridinium chloride, nickel chloride and potassium thiocyanate, present together, did not interfere with the determination of pyridine. For this purpose, a standard solution of purified pyridine was prepared by weight. Aliquots of this aqueous solution were titrated in the presence of potassium thiocyanate and nickel chloride, both in the presence and absence of pyridinium chloride. The procedure in Appendix VI was used. The results are in Table VII.

It is assumed that other metals likewise would not interfere. Similar results would be expected for the picolines.

2. Thiocyanate in Acueous Solutions

It was necessary to determine total thiocyanate in the aqueous phase of metal pyridine (and picoline) thiocyanate extraction systems. The argentimetric method (28) for thiocyanate (or chloride) was chosen.

In the solvent-extraction systems studied (see Appendix IV) the metal always was added as the dichloride salt. It is shown later that metal pyridine chlorides were not extracted into chloroform. When the aqueous phase of the solvent-extraction system was titrated in the

* Typical titration curves for pyridinium chloride versus a standard solution of sodium hydroxide are shown in Appendix X.

TABLE VI

Accuracy and precision of the potentiometric determination both of pyridine and pyridinium chloride together in aqueous solutions

Sample size : 25 ml.
Titrants : Standard aqueous solutions of hydrochloric acid and carbonate-free sodium hydroxide.
Procedures : See Appendices VI and X.

Test solution	Titrant molarity		Increments of titrant near end point, ml.		Pyridinium chloride, mg			Pyridine, mg		
	HCl	NaOH	HCl	NaOH	Taken	Found*	Sx	Taken	Found*	Sx
0.1 M Pyridine 0.1 M Pyridinium chloride	0.1	0.1	0.5	0.1	185.1	185.3	0.1	149.0	149.1	0.5
0.1 M Pyridine 0.001 M Pyridinium chloride	0.1	0.025	0.5	0.1	3.23	3.61	0.03	204.3	204.1	0.3
0.001 M Pyridine 0.1 M Pyridinium chloride	0.025	0.1	0.2	0.1	287.9	287.8	0.4	2.29	2.47	0.06

* Means of 5 replicates.

TABLE VII

The effect of nickel chloride, potassium thiocyanate and pyridinium chloride on the potentiometric determination of pyridine in aqueous solutions

Sample size : 25 ml.
Titrant : Standard aqueous solution of hydrochloric acid (0.025 M).
Procedure : See Appendix VI.

Molarities of components in test solution				Pyridine, mg		
Pyridine	Nickel chloride	Potassium thiocyanate	Pyridinium chloride	Taken	Found*	Sx
0.0007	0.005	0.3	0	1.61	1.60	0.05
"	0.005	"	0.001	"	1.59	0.04
"	0.0005	"	0	"	1.60	0.03
"	0.0005	"	0.001	"	1.64	0.03

* Means of 4 replicates.

argentimetric method, it was the sum of the chloride and the thiocyanate that was measured. However, the initial metal content of the extraction system was always known, so that the chloride content of the equilibrated aqueous phase was also known. Therefore the thiocyanate concentration of the aqueous phase could be found by difference.

In order to determine the sum of the chloride and thiocyanate concentrations, Fajans' method (28) was first considered since it involved direct titration with silver nitrate, dichlorofluorescein being the indicator. However, some thiocyanate concentrations were below 0.005M, which was the lower limit of usefulness of this method. Therefore, the Volhard method (28) was adopted. In it, the thiocyanate plus chloride were precipitated together, by the addition of a known amount of silver nitrate. The excess silver nitrate was then titrated with standard thiocyanate solution, using ferric alum as the indicator. The details of the method are in Appendix VII.

The accuracy and precision of the Volhard method were estimated. Thus, aliquots of a standard solution of potassium thiocyanate were diluted volumetrically. Replicate samples from these latter solutions were assayed for thiocyanate, by using the procedure in Appendix VII. The results are in Table VIII. Also included in the same table are some other results, which show that neither nickel nitrate nor pyridine (or picoline) interfered in the determination. Kolthoff and Sandell (74) have pointed out that a small titration error occurs when chloride and thiocyanate are titrated together by the Volhard method because of the metathesis of the silver chloride to silver thiocyanate in the vicinity of the end point. Swift and co-workers (50) found that this

TABLE VIII

Accuracy and precision of the Volhard determination of thiocyanate in aqueous solutions

Sample size : 25 ml.
Titrant : Standard aqueous solution of potassium thiocyanate.
Procedure : See Appendix VII.
Volume of titrated solution : 35 - 55 ml.

No.	Thiocyanate molarity	Silver nitrate molarity	Titrant molarity	Thiocyanate, mg		
				Taken	Found*	Sx
1	0.1	0.1	0.1	232.8	232.7	0.3
2	0.01	0.025	0.025	23.28	23.23	0.07
3	0.001	"	"	2.33	2.28	0.05
4	"	"	"	"	2.28	0.04
5	"	"	"	"	2.27	0.06
6	"	"	"	"	2.29	0.05
7	"	"	"	"	2.26	0.04

* Means of 5 replicates.

NOTES: (1) Solutions 4, 5, 6 and 7 were also 0.005 M in nickel nitrate.

(2) Solutions 4, 5, 6 and 7, respectively, were also 1.0 M in pyridine, 2-picoline, 3-picoline and 4-picoline.

metathesis introduced an error of -0.68 percent into the Volhard determination of 0.03-M chloride; they employed a procedure nearly identical to that used in the present investigation (see Appendix VII). Each aqueous sample taken from the solvent-extraction systems, and then analysed for the sum of the chloride and the thiocyanate, was 0.3M in thiocyanate and not more than 0.01M* in chloride. Even a -5.0 percent error in the portion of the titer due to chloride would only result in a -0.16 percent error in the sum of the chloride and the thiocyanate; therefore, the titration error due to this metathesis was neglected.

3. Pyridine or Picoline in Chloroform Solutions

It was necessary to determine the pyridine (or picoline) content of the equilibrated chloroform phase of metal pyridine (or picoline) thiocyanate extraction systems.

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* Since the maximum concentration of metal in the aqueous phase was 0.005M, the maximum chloride concentration of that phase was 0.01M.

NOTE: Pyridine was found to interfere seriously in the determination of 0.1-M chloride or 0.1-M thiocyanate by Fajans' method, if present in concentrations exceeding 0.005M for chloride and 0.02M for thiocyanate. In these titrations, dichlorofluorescein was the indicator, and approximately 0.1 g of dextrin was used as an anticoagulant. When pyridine was present, the end point was not observed. The interference was not avoided by over-running the theoretical end point and then back-titrating either in the presence or absence of dextrin. Addition of the dextrin and indicator just prior to the theoretical end point did not permit the indicator to function properly, nor did omission of the dextrin altogether.

However, experiments showed that the interference by pyridine (and picolines) could be eliminated if the aqueous pyridine (or picoline) solution of chloride or thiocyanate was boiled for 10 minutes prior to titration of the cooled solution with silver nitrate. The accuracy of the method then proved to be excellent.

The potentiometric determination of pyridine in chloroform, with a standard solution of perchloric acid in dioxane, has been described by Pifer, Wollish and Schmall (30,31). A glass-calomel electrode pair was used. Detection of the end point by using methyl red as an indicator also has been reported (32). The potentiometric method was chosen for the present investigation, because colored solutions were expected. The detailed procedure is in Appendix VIII. This procedure was also expected to be satisfactory for the picolines.

The accuracy and precision of the method were estimated. At the same time additional information was obtained on the pyridine and the picolines used. Thus, chloroform solutions of purified pyridine and of the purified picolines were prepared by weight. Aliquots of these solutions were diluted volumetrically*, then replicates were titrated by the potentiometric procedure in Appendix VIII. The results are in Table IX. Typical titration curves for pyridine are shown in Fig. 8. The titration curves for the picolines were similar. However, in practice, the end points were always found algebraically by the method of second differences (49).

Fritz (32) pointed out that 0.1-M solutions of perchloric acid in dioxane were stable for a period of several weeks. It was found, in the present investigation, that 0.025-M solutions had become unstable during 3-4 weeks' storage; the meter readings were erratic and the end points could no longer be found.

The chloroform phase of an equilibrated metal pyridine (or

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* Chloroform solutions of pyridine (or picoline) were found to become discolored if left for a week, even in the dark; but the titers of 0.1-M and even 0.001-M solutions were not measurably changed during a storage period of 2 weeks.

TABLE IX

Accuracy and precision of the potentiometric determination of pyridine and the picolines in chloroform solutions

Sample size : 25 ml.
Titrant : Standard solution of perchloric acid in dioxane (0.025 M).
Procedure : See Appendix VIII

Test solution	No. of replicates	Increments of titrant near end point, ml	Pyridine or Picoline, mg		
			Taken	Found*	Sx
0.03 M Pyridine	5	0.1	81.9	81.8	0.0
0.03 M 2-Picoline	3	0.1	107.0	106.8, 106.9, 106.9	-
0.03 M 3-Picoline	2	0.1	94.1	93.8, 93.8	-
0.03 M 4-Picoline	2	0.1	114.1	113.8, 113.9	-
0.003 M Pyridine	5	0.05	8.19	8.19	0.02
0.0006 M Pyridine	5	0.05	1.63	1.62	0.00

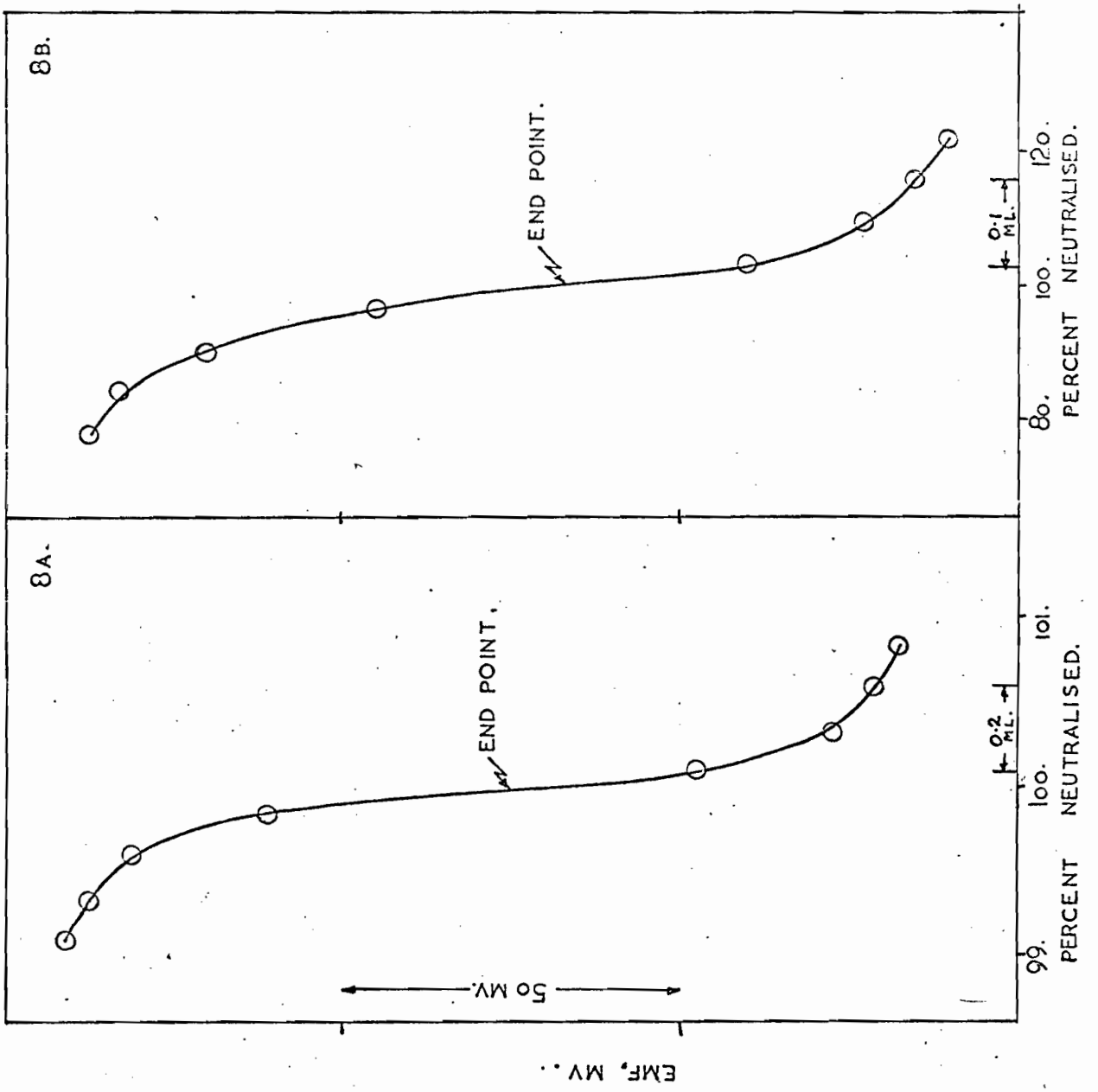
* Means of replicates, except for picolines.

FIGURE 8

Typical potentiometric titration curves for the determination of pyridine in chloroform solutions.

(A) 0.03-M pyridine vs 0.025-M perchloric acid in dioxane.

(B) 0.0006-M pyridine vs 0.025-M perchloric acid in dioxane.


8B.
END POINT.
0·1 ML.
80.
100.
120.
PERCENT NEUTRALISED.
8A.
END POINT.
0·2 ML.
99.
100.
101.
PERCENT NEUTRALISED.
50 MV.
EMF, MV.

picoline) thiocyanate extraction system contained not only free pyridine (or picoline) but also the metal pyridine (or picoline) thiocyanate complex. Therefore, it was important to determine whether or not the pyridine (or picoline) in this complex was quantitatively titrated by the potentiometric method. Thus, a 0.1-M solution of pyridine in chloroform was prepared. Four 10-ml aliquots were titrated according to the procedure in Appendix VIII; two aliquots contained 30 mg of nickel tetrapyridine thiocyanate*, and the other two contained none. The two aliquots containing the metal complex required, respectively, 12.7 ml and 12.5 ml more of the 0.025-M perchloric acid in dioxane. These volumes correspond to 68.4 percent and 67.8 percent, respectively, of pyridine in the metal complex; the theoretical value was 64.5 percent. It was concluded that the pyridine in the complex had been quantitatively titrated. It was expected that similar results would be obtained if either the other metal pyridine thiocyanates or the metal picoline thiocyanates were tested in the same way.

The discrepancy between the expected (64.5) and the observed (68.4 and 67.8) percentages of pyridine in the complex, and also the spread in the duplicates, require comment. When metal complex was present, meter readings were somewhat unstable during the titration. As a result, the end points could not be determined as precisely or as accurately as was the case for the titrations reported in Table IX. This lack of precision is illustrated by the results in Tables XIV and XXIX where pyridine was titrated in the presence of nickel pyridine thiocyanate. The

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* This complex salt was prepared by Miss G. Simmons of this laboratory. Its purity was confirmed, by the author, through analysis for thiocyanate (23.65 percent expected, 23.63 percent found) and for nickel (11.95 percent expected, 11.96 percent found). See Part IV-4 and Part IV-5 for details.

interference of the metal complex in the titration may be related to the fact that, during the titration of pyridine with perchloric acid, insoluble nickel thiocyanate was precipitated from the chloroform solution.

4. Thiocyanate in Chloroform Solutions

The total thiocyanate concentration was required in the equilibrated chloroform phases of metal pyridine (and picoline) thiocyanate extraction systems.

The procedure chosen (Appendix IX) consisted first of evaporating the solvent, then of determining the thiocyanate in an aqueous extract of the residue, by the conventional Volhard method.

The accuracy and precision of the method were estimated as follows: 3.24 g of nickel tetrapyridine thiocyanate* were dissolved in a 0.1-M solution of pyridine in chloroform. The resulting solution was diluted exactly to 500 ml, and three 25-ml aliquots were then carried through the procedure given in Appendix IX. The results were: 38.24 mg, 38.29 mg, and 38.33 mg of thiocyanate (SCN) found; the expected value was 38.30 mg.

5. Nickel in Aqueous and Chloroform Solutions

In order to find the distribution ratios for nickel in equilibrated nickel pyridine (or picoline) thiocyanate extraction systems, procedures were necessary for the determination of nickel both in aqueous and in chloroform solutions. A complexometric titration with ethylenediamine-

* This complex salt was prepared by Miss G. Simmons of this laboratory. Its purity was confirmed, by the author, through analysis for pyridine (64.5 percent expected, 68.1 percent found) and for nickel (11.95 percent expected, 11.96 percent found). See Part IV-3 and Part IV-5 for details.

tetraacetic acid (EDTA) was used to determine nickel in concentrations down to about 0.001M; below that concentration, a colorimetric method with dimethylglyoxime was used. These methods are described below.

5-1. Complexometric Titration of Nickel

Harris and Sweet (38) described the direct titration of nickel in aqueous solution, by using EDTA as the titrant and Murexide as the indicator. Their procedure was adopted, and is recorded in Appendix XI, Procedure A.

The accuracy and precision of the method were estimated. Thus, a solution of nickel chloride was standardized by Procedure A in Appendix XI. Aliquots of this standard solution were diluted volumetrically. Then replicate samples of each solution were titrated. In addition, one solution was titrated both in the presence and in the absence of a mixture of thiocyanate and either pyridine or a picoline. All of the results are in Table X. It is evident that thiocyanate did not interfere, even in the presence of pyridine or a picoline.

In order to analyse chloroform solutions for nickel, the chloroform was evaporated, the residue was dissolved in water and the nickel was determined as described above for aqueous solutions. The accuracy and precision were estimated for this procedure (Procedure B, Appendix XI). Weighed amounts (three samples) of nickel tetrapyridine thiocyanate* were dissolved in approximately 100 ml of a 0.1-M solution

* This complex salt was prepared by Miss G. Simmons of this laboratory. Its purity was confirmed, by the author, through analysis for pyridine (64.5 percent expected, 68.1 percent found) and for thiocyanate (23.65 percent expected, 23.63 percent found). See Part V-3 and Part V-4 for details.

TABLE X

Accuracy and precision of the complexometric determination of nickel in aqueous solutions

Sample size : 50 ml.
Titrant : Standard aqueous solution of EDTA (0.01M)
Procedure : See Appendix XI, Procedure A.

No.	Nickel molarity	Nickel, mg		
		Taken	Found*	Sx
1	0.008	22.76	22.76	0.03
2	0.0015	4.55	4.58	0.02
3	0.0006	1.82	1.84	0.02
4	0.0003	0.96	0.98	0.02
5	"	"	0.97	0.02
6	"	"	0.99	0.02
7	"	"	0.97	0.02

* Means of 5 replicates.

NOTES: (1) Solutions 4, 5, 6 and 7 were also 0.3M in thiocyanate.

(2) Solutions 4,5,6 and 7, respectively, were also 0.1M in pyridine, 2-picoline, 3-picoline and 4-picoline.

of pyridine in chloroform. The nickel was determined by carrying each solution through Procedure B of Appendix XI. The results were as follows: 26.52 mg, 21.68 mg, and 18.83 mg of nickel (as Ni) were expected for the three samples, respectively; 26.46 mg, 21.77 mg, and 18.83 mg, respectively, were found.

5-2. Colorimetric Determination of Nickel

In order to determine nickel colorimetrically, the dimethylglyoxime-bromine procedure of Makepeace and Craft (33,35) was tested. This method proved to be unsatisfactory, because the color stability and precision of results were poor.

The colorimetric procedure of Claassen and Bastings (34,35) using dimethylglyoxime was then tried. This procedure utilizes persulphate as the oxidizing agent, in strongly basic solution. Color development is too slow at room temperature; the solution must be heated at 60-70°C. Once developed, the color is said (35) to be stable for 24 hours*. This procedure, recorded in Appendix XII, was found to be satisfactory for up to 300 μg of nickel. Beer's Law was found to be obeyed.

However, it was found that the presence of 0.1-M thiocyanate caused color development to be incomplete. Moreover, the color rapidly faded. Therefore, metal pyridine (or picoline) thiocyanate extraction systems could not be analysed directly by the method. However, oxidation of the thiocyanate with hot nitric acid, using the procedure recorded in Appendix XIII, proved a satisfactory way of eliminating this interference. Rosanoff and Hill (36) and later Bruckmiller (37) destroyed thiocyanate

* The color was found, in this laboratory, to be stable for 36 hours.

in this way. Chloride is not affected (37), and may subsequently be titrated by the conventional Volhard method (28).

Pyridine proved not to interfere in the determination. In addition, the substitution of nitric acid for hydrochloric acid in the procedure caused no change in the observed results. Therefore, small amounts of nitric acid that may remain after oxidation of the thiocyanate (Appendix XIII) would have no effect when carried through the colorimetric procedure (Appendix XII).

Further experiments showed that the procedure used for the oxidation of thiocyanate caused volatilization of some nickel, regardless of whether or not thiocyanate and pyridine were initially present. These experiments are described below. The results are in Table XI.

In experiment 1, a known weight of nickel was carried through the colorimetric procedure (Appendix XII).

In experiments 2, 3 and 4, samples of nickel which contained 0, 0.001 and 0.005 mole, respectively, both of pyridine and thiocyanate were carried through the oxidation procedure* (Appendix XIII), then through the colorimetric procedure (Appendix XII).

Experiment 5 was identical to experiment 3, except that the final evaporation in the oxidation procedure* was carried to near dryness on an asbestos-covered hot plate. Experiment 6 was identical to 3 except that the final evaporation in the oxidation procedure* was carried to complete dryness on an asbestos-covered hot plate.

In experiment 7 a known amount of nickel was carried through this

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* This procedure involved two evaporations of the sample, each with 15 ml of 6.0-M nitric acid. Both evaporations were carried to 4-5 ml on a hot plate. The remainder of the nitric acid was then evaporated on a steam bath (final evaporation step).

TABLE XI

Effect of the oxidation procedure (Appendix XIII) on the colorimetric determination of nickel (Appendix XII)

Expt. No.	Reagent added, mole		Nickel, µg		
	Pyridine	Thiocyanate	Taken	Found*	Sx
1	0	0	109.0	109.0	0.4
2	0	0	"	105.8	0.9
3	0.001	0.001	"	104.9	0.8
4	0.005	0.005	"	103.3	1.2
5	0.001	0.001	"	100.0	0.7
6	0.001	0.001	"	97.4	2.0
7	0.001	0.001	1090.	1089.	4.0

* Means of 5 replicates.

oxidation procedure. One-tenth of the treated (oxidized) sample was then carried through the colorimetric procedure.

A statistical treatment* of the data was then made: thus, comparison of experiments 1 and 2 showed that loss (presumably volatilization) of nickel had occurred in the latter case. Experiments 3, 5 and 6 showed that the degree of volatilization depended on the evaporation conditions in the oxidation procedure. Comparison of both experiments 2 and 4 with experiment 3 showed that the amount of nickel recovered was not** a function of the initial concentration of thiocyanate and pyridine. Experiment 7 showed that the percentage loss was low when a 1-mg sample was carried through the oxidation procedure. Consequently, when an aliquot of the treated sample was analysed colorimetrically, no loss could be detected. In other words, the oxidation procedure had no apparent effect. The reason for this anomaly is not clear.

In order to analyse one or both of the phases of extraction systems, 25-ml aliquots were carried through the oxidation procedure***. Then, if the aliquot contained less than 300 μg of nickel, it was carried directly through the colorimetric procedure. The calibration curve was prepared from known amounts of nickel carried through both the oxidation

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* The t-test of significance (63) for the difference between means was used.

** The means were not different as shown by the t-test of significance (63).

*** An aliquot contained 0-4 mg of nickel, some pyridine or picoline, and not more than 0.007 mole of thiocyanate. It was assumed, for chloroform solutions, that the simple step of evaporating the solvent, prior to the oxidation step, would not interfere. It is later shown (see Part V-3) that the chloroform reagent was free from nickel.

and the colorimetric procedures.

If the oxidized sample contained more than 300 μg of nickel, the solution was diluted to 100 ml and an aliquot taken for the colorimetric analysis. It has been shown that volatilization losses caused by the oxidation procedure are not apparent at the 1-mg level (see Table XI, experiment 7). Therefore, the calibration curve in this case was prepared as follows: amounts of nickel between 0.4 and 4 mg were carried through the oxidation procedure. A fraction of each resulting sample was then carried through the colorimetric procedure.

6. Cobalt in Aqueous and Chloroform Solutions

Determination of the distribution ratios of cobalt in equilibrated cobalt pyridine (or picoline) thiocyanate extraction systems required procedures for cobalt both in aqueous and in chloroform solutions. A complexometric method using ethylenediaminetetraacetic acid (EDTA) as titrant, and a colorimetric procedure using Nitroso-R salt were investigated. They are described below.

6-1. Complexometric Titration of Cobalt

The titrimetric determination of cobalt with EDTA is known (39, 40). The micro-method of Flaschka (40,41) was tested for precision. This method involves a direct titration of cobalt solutions with EDTA, with Murexide as indicator. However, the method proved not to be sufficiently precise for the present purpose. For example, the standard deviation was 2.0×10^{-5}M when four samples of a 1.0×10^{-4}-M solution of cobalt were titrated.

Nevertheless, stock solutions of cobalt could be, and were

standardized by the conventional macro-titration with EDTA, by using Murexide as the indicator (39).

6-2. Colorimetric Determination of Cobalt

Sandell (42) has reported several methods for the colorimetric determination of cobalt. One method (43) involved color development with Nitroso-R salt in a slightly acid, buffered solution. After color development, excess reagent was removed by boiling with nitric acid. The color was stable for 12 hours.

It was found in the present work that reproducibility of the method was improved if the pH of the buffer solution was adjusted with the aid of a pH meter, rather than with the aid of an indicator (brom-cresol green). This procedure is in Appendix XIV.

Tests of this procedure showed that Beer's Law was obeyed, at least up to 350 μg. Moreover, the presence of 0.002 mole of pyridine did not interfere. However, cobalt samples taken from extraction systems contained not only pyridine (or picoline) but also thiocyanate. Since this thiocyanate would be oxidized by nitric acid in the procedure (Appendix XIV), it was removed before carrying out the colorimetric procedure, by using the procedure given in Appendix XIII*.

Experiments showed that when thiocyanate (and pyridine) were present, the oxidation procedure of Appendix XIII led to a positive error in the cobalt determination. A reagent blank was carried through each experiment. The results are in Table XII. Each of the experiments is

* This procedure involved two evaporations of the sample, each with 15 ml of 6.0-M nitric acid. Both evaporations were carried to 4-5 ml on a hot plate. The remainder of the nitric acid was then evaporated on a steam bath (final evaporation step). This procedure is also discussed in Part IV-5-2.

TABLE XII

Effect of pyridine and thiocyanate on the colorimetric determination of cobalt by Nitroso-R salt

Expt. No.	Number of replicates	Reagent added, mole		Cobalt, µg		
		Pyridine	Thiocyanate	Taken	Found*	Sx
1	10	0	0	108.6	108.6	0.7
2	3	0	0	108.6	108.8	0.3
3	3	0	0	43.5	43.3	0.3
4	3	0.002	0.0002	108.6	108.8	0.5
5	3	0.002	0.0002	43.5	43.3	0.4
6	8	0.002	0.007	108.6	113.0	0.7
7	5	0.002	0.007	43.5	45.3	0.4

* Means of replicates.

described below.

Experiments 1 and 3 were for the purpose of calibration; known amounts of cobalt were carried through the colorimetric procedure. In experiment 2, the oxidation procedure was interpolated.

In experiments 4 and 5, known amounts of cobalt, in the presence of 0.002 mole of pyridine and 0.0002 mole of thiocyanate were carried first through the oxidation procedure, then through the colorimetric procedure.

Experiments 6 and 7 were identical to 4 and 5 respectively, except that 0.007 mole of thiocyanate was initially present.

A statistical treatment* of the data was then made: thus, comparison of experiments 1 and 2 showed that the oxidation procedure itself had no measurable effect on the recovery of cobalt. Comparison of experiments 1 and 3 with experiments 4 and 5, respectively, showed that the initial presence of 0.002 mole of pyridine and 0.0002 mole of thiocyanate had no measurable effect on cobalt recovery. However, comparison of experiments 1 and 3 with experiments 6 and 7, respectively, showed that the initial presence of 0.002 mole of pyridine and 0.007 mole of thiocyanate introduced a positive error into the colorimetric analysis.

In order to analyse one or both of the phases of extraction systems, 25-ml aliquots were carried through the oxidation procedure**.

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* The t-test of significance (63) for the difference between means was used.

** An aliquot contained 0-4 mg of cobalt, some pyridine (or picoline) and thiocyanate (not more than 0.0002 mole for chloroform samples and not more than 0.007 mole for aqueous samples). It was assumed, for chloroform solutions, that the simple step of evaporating the solvent, prior to the oxidation step, would not interfere. It is later shown (see Part V-3) that the chloroform was free from cobalt.

The chloroform samples contained not more than 0.0002 mole of thiocyanate; the initial presence of this amount of thiocyanate had been shown not to affect the analysis, provided that the oxidation procedure had first been carried out. Therefore, a calibration curve that was obtained by carrying known amounts of cobalt in an aqueous solution through the colorimetric procedure was used in the analysis of samples from the chloroform phases.

The aliquots from the aqueous phases contained about 0.007 mole of thiocyanate; the initial presence of this amount of thiocyanate had been shown to introduce a positive error* into the colorimetric analysis. Thus, a calibration curve was prepared as follows: known amounts of cobalt, in the presence of 0.007 mole of thiocyanate were first carried through the oxidation procedure (Appendix XIII), then through the colorimetric procedure. Beer's Law was obeyed. This calibration curve was used in the analysis of 25-ml aliquots from the aqueous phases that contained not more than 350 µg of cobalt. If more than 350 µg was present in the aliquot then, after completion of the oxidation procedure, an aliquot was taken for the colorimetric procedure. Because this aliquot contained correspondingly less of the interfering

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* The error may be due to the presence of traces of unoxidized thiocyanate; the cobalt salt may have a higher absorptivity than that of the cobalt Nitroso-R salt complex. This possibility, although not investigated further, was supported by the fact that the positive error in the colorimetric analysis was proportional to the cobalt concentration (see Table XII).

component, then a correction* was applied to the measured absorbance. The calibration curve was then used to determine the cobalt content of the aliquot.

7. Zinc or Cadmium in Aqueous and Chloroform Solutions

Determination of the distribution ratios of zinc (or cadmium) in equilibrated zinc (or cadmium) pyridine and picoline thiocyanate extraction systems required procedures for zinc (or cadmium) both in aqueous and in chloroform solutions.

The determination of zinc or cadmium in aqueous solutions by titration with ethylenediaminetetraacetic acid (EDTA) is well known (41, 44,45,46); the method of Biedermann and Schwarzenbach (44) was chosen for the purpose of the present investigation, since it involved a direct titration with EDTA with Eriochrome Black T as the indicator. The details of the method are in Appendix XV, Procedure A.

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* For example, a cobalt sample of 108.6 μg that contained no added thiocyanate gave an absorbance of 0.413. The same weight of cobalt, in the presence of 0.007 mole of thiocyanate, was carried first through the oxidation procedure, then through the colorimetric procedure. The absorbance was 0.430. Now suppose a 1086-μg sample of cobalt, containing 0.007 mole of thiocyanate, is carried through the oxidation procedure. A fraction of this sample must be used in the colorimetric procedure. If one-tenth (108.6 μg) of the sample were to be taken for the colorimetric procedure then the absorbance would be between 0.430 and 0.413 because less of the interfering component would be present. The correction applied to the absorbance read would then be + (0.430 - 0.413) (1 - Fraction taken for colorimetric analysis).

The validity of this correction was checked by experiment: a 1086-μg sample of cobalt, containing 0.007 mole of thiocyanate was carried through the oxidation procedure. The residue was dissolved in exactly 100 ml of water. Aliquots of 10 ml were then carried through the colorimetric procedure. The correction was applied to the absorbance reading. Result: 108.6 μg expected, 108.8 μg found (mean of 4 replicates).

The accuracy and precision of the method were estimated. Thus, solutions of zinc chloride and of cadmium chloride were standardized according to Procedure A in Appendix XV. Aliquots of these standard solutions were diluted volumetrically. Then replicate samples of each solution were titrated. In addition, solutions were titrated in the presence both of thiocyanate and either pyridine or a picoline. All of the results are in Table XIII. It is evident that the presence of thiocyanate and either pyridine or a picoline did not interfere.

In order to determine the zinc or cadmium concentration in chloroform solutions the method in Appendix XV, Procedure B was used. This method involved evaporation of the solvent, then titration of the dissolved residue with EDTA, as described above for aqueous solutions. It was assumed that the simple step of evaporating the chloroform would not interfere. It is later shown (see Part V-3) that the chloroform reagent was free from both zinc and cadmium.

TABLE XIII

Accuracy and precision of the complexometric determination of zinc and of cadmium in aqueous solutions

Sample size : 50 ml.
Titrant : Standard aqueous solution of EDTA (0.01 M).
Procedure : See Appendix XV, Procedure A.

No.	Zinc			
	Metal molarity	Taken, mg	Found*, mg	Sx
1	0.005	15.20	15.20	0.03
2	0.001	3.04	3.03	0.02
3	0.00025	0.76	0.75	0.02
4	0.0001	0.30	0.30	0.01
5	"	"	0.30	0.01
6	"	"	0.30	0.01
7	"	"	0.31	0.01
8	"	"	0.30	0.01
	Cadmium			
9	0.001	6.43	6.42	0.07
10	0.0005	2.57	2.55	0.02
11	0.0001	0.51	0.50	0.02
12	"	"	0.51	0.02
13	"	"	0.51	0.01
14	"	"	0.50	0.02
15	"	"	0.51	0.02

* Means of 4 replicates.

NOTES: (1) Solutions 5 - 8 and 12 - 15, inclusive, were also 0.3 M in thiocyanate.
(2) Solutions 5 and 12 were also 0.1 M in pyridine.
(3) Solutions 6 and 13 were also 0.1 M in 2-picoline.
(4) Solutions 7 and 14 were also 0.1 M in 3-picoline.
(5) Solutions 8 and 15 were also 0.1 M in 4-picoline.

PART V

EXPERIMENTAL RESULTS

1. Introduction

Part V is separated into four sections. The purpose of each section is outlined below.

Part V-1 summarizes the analytical procedures used to determine metal, pyridine (or picoline) and thiocyanate in the solvent-extraction systems. In addition, several distribution ratios were evaluated in order to show that these procedures were sufficient for the present investigation.

Part V-2 describes exploratory extractions carried out in order to ascertain approximately the maximum concentration of metal possible in a given extraction system, without separation of a solid phase.

In Part V-3 estimates are given of the accuracy and precision both of the extraction and the analytical procedures. In addition, equilibrium is shown to be rapidly established in the extraction systems. Moreover the equilibrium point in extraction systems of this kind is shown to be very temperature dependent. The ethanol normally present as a preservative in chloroform is shown to have no measurable effect on the distribution of the metal pyridine (or picoline) thiocyanates. The distribution ratios of metal chlorides (and thiocyanates), metal pyridinium (or picolinium) chlorides (and thiocyanates) and metal pyridine (or picoline) chlorides are shown to be smaller than the sensitivity of the analytical methods; these ratios could then be safely ignored. Small variations in the thiocyanate concentration of the aqueous phase were shown, for selected extraction systems, to have no measurable effect on the distribution ratio of the metal.

Part V-4 contains the main part of the experimental data. This

data included the measured distribution ratios of cobalt, nickel, zinc and cadmium between chloroform and aqueous thiocyanate solutions, as the equilibrium concentration of pyridine (or picoline) was varied while that of thiocyanate was constant.

1-1. Summary of Extraction and Analytical Procedures

Unless otherwise noted, the extractions reported in Part V-3 and Part V-4 were carried out according to the procedure in Appendix IV.

Methods for the chemical analysis of metal pyridine (and picoline) thiocyanate extraction systems are summarized below. They have been discussed in Part IV. Details of each method are in the Appendices noted in brackets.

Pyridine or Picoline (Appendices VI and VIII)

A sample from the aqueous phase of each extraction system was titrated potentiometrically with a standard solution of hydrochloric acid. A sample from the chloroform phase* was titrated potentiometrically with a standard solution of perchloric acid in dioxane.

Thiocyanate (Appendices VII and IX)

The aqueous and chloroform phases of an extraction system were assayed for thiocyanate by adding a slight excess of silver nitrate to the acidified solution**. The excess silver was then titrated with a

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* The chloroform phase was analysed only during the study of nickel pyridine thiocyanate extraction systems (see Part V-3-1 for details).

** In the case of chloroform solutions, the solvent was first evaporated. Then the residue was dissolved in water. The solution was then acidified and an excess of silver nitrate was added.

standard solution of potassium thiocyanate using ferric alum as the indicator.

Nickel (Appendices XI and XII)

Three initial concentrations of nickel (0.005M, 0.0025M and 0.0005M) were used during the study of nickel pyridine thiocyanate extraction systems. An initial nickel concentration of 0.005M was used in the nickel picoline thiocyanate systems. For systems that had initial concentrations of nickel of 0.0025M or 0.0005M, both phases were assayed colorimetrically (using dimethylglyoxime) by the procedure in Appendix XII. For systems having an initial concentration of nickel of 0.005M, the equilibrated phase that contained the smaller concentration of nickel was also assayed colorimetrically by the above procedure; the other phase was assayed by titration with a standard solution of ethylenediaminetetraacetic acid using Murexide as the indicator (Appendix XI).

Cobalt (Appendix XIV)

Both phases of cobalt pyridine (and picoline) thiocyanate extraction systems were assayed colorimetrically by using Nitroso-R salt.

Zinc or Cadmium (Appendix XV)

Both phases of zinc (and cadmium) pyridine (and picoline) thiocyanate extraction systems were assayed by titration with a standard solution of ethylenediaminetetraacetic acid using Eriochrome Black T as the indicator.

1-2. Evaluation of Some Distribution Ratios

In order to show that additional analytical methods were unnecessary to the study of the specified solvent extraction systems, several distribution ratios were evaluated.

It was expected that the metal pyridine (or picoline) thiocyanate complex, together with an excess of pyridine (or picoline) would be extracted into the chloroform phase. However, information was not available in the literature concerning either the solubility in chloroform or the distribution ratio between chloroform and water of the following reagents: potassium thiocyanate, thiocyanic acid, pyridinium (or picolinium) thiocyanate, hydrochloric acid, and pyridinium (or picolinium) chloride. Therefore, some of the se distribution ratios were measured. The methods and the results are now described.

(a) Hydrochloric Acid

Concentrated (12M) hydrochloric acid was shaken vigorously, at room temperature, with an equal volume of reagent-grade chloroform. The chloroform phase was separated, then shaken with an acidified aqueous solution of silver nitrate. Neither a precipitate, nor a turbidity was observed. It was also found that a 10^{-5}-M aqueous solution of chloride gave a turbidity when treated with the same silver nitrate solution. Therefore, the distribution ratio of hydrochloric acid between chloroform and water was less than 8×10^{-7}.

(b) Thiocyanic Acid

An aqueous 0.5-M solution of thiocyanic acid was shaken vigorously,

at room temperature, with an equal volume of reagent-grade chloroform. The chloroform phase was separated, then shaken with an aqueous solution of sodium hydroxide in order to extract the thiocyanate from the chloroform. A small excess of standard silver nitrate was added to the aqueous extract together with [illegible] of nitric acid. This solution was titrated* with a standard potassium thiocyanate solution using ferric alum as the indicator. The distribution ratio of thiocyanic acid between chloroform and water was found to be 4.7×10^{-3}.

The concentration of thiocyanate in the chloroform phase of the extraction system described above was also found by a color-comparison method. The separated chloroform phase was shaken with an aqueous solution of ferric chloride. The characteristic red color that formed in the aqueous phase was compared visually with a series of standards. The distribution ratio of thiocyanic acid between chloroform and water was thus found to be 5.0×10^{-3}.

(c) Pyridinium Chloride

An aqueous 1.0-M solution of pyridinium chloride was shaken vigorously, at room temperature, with an equal volume of reagent-grade chloroform. The chloride concentration of the chloroform phase was found as described above, in (a), for hydrochloric acid. The distribution ratio of pyridinium chloride between chloroform and water was thus found to be less than 10^{-5}.

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* See Appendix VII for a detailed procedure.

(d) Pyridinium thiocyanate

An aqueous 0.1-M solution of pyridinium thiocyanate* was shaken vigorously, at room temperature, with an equal volume of reagent-grade chloroform. The thiocyanate concentration of the separated chloroform phase was determined by the color-comparison method described above, in (b), for thiocyanic acid. The distribution ratio of pyridinium thiocyanate between chloroform and water was thus found to be 1.0×10^{-3}.

(e) Conclusions

The extraction into the chloroform phase of hydrochloric acid, pyridinium chloride, thiocyanic acid, and pyridinium thiocyanate could be neglected, for the metal pyridine thiocyanate extraction systems. The reason is that the concentrations of these species in the aqueous phase were in practice too low to allow significant extraction. For example, the concentration of thiocyanic acid and of pyridinium thiocyanate in the aqueous phase of a metal pyridine thiocyanate extraction system did not exceed 10^{-4} M and 10^{-3} M, respectively.

It was assumed that the above findings for pyridine would also hold for the picolines.

Evidence is also presented later, showing that the chloroform phase of a metal pyridine (or picoline) thiocyanate extraction system contained only the metal pyridine (or picoline) thiocyanate complexes,

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* An aqueous 0.20-M solution of thiocyanic acid was prepared (47) by adding the calculated quantity of sulphuric acid to an aqueous solution of barium thiocyanate and then filtering off the precipitated barium sulphate. This solution was added to an equal volume of aqueous 0.25-M pyridine.

together with an excess of pyridine (or picoline).

2. Exploratory Study of Metal Pyridine and Picoline Thiocyanate Extraction Systems

An equilibrium distribution study of the pyridine (and picoline) thiocyanates of cobalt, nickel, copper, zinc and cadmium was carried out. The purpose was to assign the experimental conditions necessary to ensure that equilibrium values of the distribution ratios of these metals would be obtained.

The extraction (into chloroform) of cobalt 2-picoline thiocyanate was considered in detail (see Parts V-3 and V-4). It was found, for example, that the equilibrated chloroform phase must contain, at 25.0°C, about 11 percent by volume of 2-picoline in order to effect 57 percent extraction of the cobalt. Semi-quantitative tests showed that similar quantities of 2-picoline were required to extract the 2-picoline thiocyanates of nickel, zinc and cadmium. These large quantities of 2-picoline essentially changed the nature of the solvent. Therefore, these systems could not reasonably be compared with pyridine, 3-picoline or 4-picoline systems, for which much smaller quantities of these reagents were needed for extraction of the metals. Therefore, the metal 2-picoline thiocyanates (with the exception of cobalt) were not further studied.

An exploratory study of the distribution of copper pyridine thiocyanate between chloroform and water revealed that a detailed study of this system was not practicable, because when insufficient pyridine was present in the system completely to extract the copper, a white precipitate

was formed at the chloroform-water interface. However, when the phases of replicate extractions were analysed for copper*, a consistent material balance could not be obtained. However, these systems contained copper which was initially added as the chloride salt, whereas other investigators (11,13) prepared this system with the nitrate salt. Their instructions were followed, but under conditions of incomplete extraction, the interfacial precipitate remained.

Britton (52) has pointed out that 0.02-M copper solutions hydrolyse at pH 5.6. Addition of pyridinium chloride lowered the pH of the equilibrated aqueous phase to pH 5. However, the interfacial precipitate and inconsistent material balance persisted.

Williams (54) noted that "pyridine should be first added to the solution of the copper salt, followed by the thiocyanate", before extraction with chloroform. These directions were followed, but the precipitate remained.

It seems probable that the precipitate was cuprous thiocyanate, known (53) to be formed when thiocyanate is added to an aqueous cupric-ion solution. This formation was prevented only when so much pyridine was present that essentially all of the cupric ion was extracted.

Because of this precipitate formation, further study of copper pyridine (and picoline) thiocyanate extraction systems was not undertaken.

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* Copper was extracted into carbon tetrachloride as the dibenzyldithiocarbamate and the absorbance of this extract was measured at 435 mμ. The detailed procedure is given by Sandell (83). It was found, in this laboratory, that the presence of pyridine and thiocyanate in the copper sample did not interfere. In order to determine the copper content of a chloroform solution, the solvent was first evaporated at room temperature. Then the residue was dissolved in 1-M hydrochloric acid and the colorimetric analysis was carried out.

Interfacial precipitates were not formed during the study of pyridine, 2-picoline, 3-picoline or 4-picoline thiocyanates of cobalt, nickel, zinc and cadmium.

The low solubility of the metal pyridine thiocyanates has previously been utilized for the gravimetric determination of these metals. Moreover, these complexes, as well as the corresponding picoline complexes have limited solubilities in either chloroform or chloroform solutions of pyridine or picoline. Therefore, these maximum concentrations of the metals were determined, such that no precipitate existed in the solvent-extraction systems at equilibrium. It was found that the following metal concentrations were about the maximum values that could safely be used in the pyridine (or picoline) thiocyanate solvent-extraction systems; nickel, 5×10^{-3} M; cobalt, 1.3×10^{-3} M; zinc, 5×10^{-3} M; cadmium, 1×10^{-3} M.

As a result of the above experiments, the pyridinates, 3-picolinates and 4-picolinates of cobalt, nickel, zinc and cadmium were selected for intensive study, although the 2-picolinate of cobalt was also studied in detail. The experimental data for these detailed solvent-extraction studies are given in the following sections.

3. Factors Affecting the Distribution of Metal Pyridine and Picoline Thiocyanates

The pyridine, 2-picoline, 3-picoline and 4-picoline thiocyanates of cobalt, nickel, zinc and cadmium were studied*. The distribution ratio

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* Of the 2-picolinates, only that of cobalt was studied in detail.

of each of these metals between chloroform and aqueous solutions of constant ionic strength* was measured as the equilibrium concentration of pyridine (or picoline) in the system was varied. A plot of the percent extraction of metal against the equilibrium concentration of pyridine (or picoline) gave a sigmoid curve. The position of this curve was unique for each of the metal pyridine (and picoline) thiocyanate extraction systems.

In order to obtain a statistical measure of the confidence that could be placed in the position of each sigmoid curve, replicate extractions were carried out for one point on each curve. From the values found for the distribution ratios of the metal, standard deviations were calculated for that point.

The effect of temperature on the extraction system was measured. Proof of equilibrium in the extraction systems was provided. The effect of ethanol** in the extraction systems was investigated. The effect of a small variation in the thiocyanate concentration of the aqueous phase was evaluated. In addition, it is shown that the metals were not measurably extracted in the absence of either thiocyanate or pyridine (or picoline).

The experiments on the above factors and the results, together with the statistical data on the replicate extractions are given below

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* This medium of constant ionic strength was provided, in each extraction system, by an aqueous phase 0.3M in thiocyanate.

** Ethanol is present in reagent-grade chloroform as a preservative. Hentzsch (71) has pointed out that metal alcoholates form in either methanol or ethanol. Therefore, the effect of ethanol in the extraction system deserved some consideration.

for each metal pyridine (and picoline) thiocyanate.

3-1. Nickel Pyridine Thiocyanate

The analytical data on the sets of replicate extractions are given in Tables XIV and XV. In Table XIV, the extractions were made from aqueous solutions 0.1M in thiocyanate*. Both phases of the extraction system were analysed for pyridine. The standard deviation for this analysis in the chloroform phase was much larger than that in the aqueous phase. This observation, together with later extraction results (Table XXVII) for this system, and the earlier discussion in Part IV-3, led to the decision not to analyse the chloroform phase of any other extraction system for pyridine (or picoline). Instead, concentrations in the chloroform phase were more accurately determined from the difference between the total amount of pyridine or picoline present in the system, and that determined by analysis of the equilibrated aqueous phase.

The results in Table XV were for extractions from aqueous solutions 0.3M in thiocyanate, and they confirm the results in Table XIV. The results in these two tables showed that a material balance was obtained for both nickel and thiocyanate. Hence, where the thiocyanate concentration of the chloroform phase was determined experimentally, or it was possible to calculate that concentration from the molar ratio of metal to thiocyanate, then the thiocyanate concentration of the aqueous

* All other quantitative extraction data for the metal pyridine (and picoline) thiocyanates were obtained by extraction from a 0.3-M thiocyanate medium.

TABLE XIV

Accuracy and precision of the combined extraction and the analytical procedures for nickel, pyridine and thiocyanate

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Component	Taken, mg (in H_2O)		Found *						D	Sx	E	Sx
			H_2O	Sx	$CHCl_3$	Sx	Total	Sx				
Nickel	27.38	mg	24.20	0.10	3.21	0.04	27.41	0.1	0.137	0.003	0.7	0.2
		M x 10^3	4.53	0.02	0.622	0.008	-					
Pyridine	81.5	mg	5.59	0.03	76.6	0.8	82.2	0.8				
		M x 10^3	0.776	0.009	11.0	0.1	-					
Thiocyanate	556.6	mg	546	2	6.4	0.1	552	2				
		M x 10^3	103.0	0.4	1.25	0.02	-					

* Mean of 5 extractions.

NOTES: (1) Equilibrium pH of aqueous phase was 6.43, Sx = 0.03.

(2) Molar ratio of thiocyanate to nickel in chloroform phase was 2.01, Sx = 0.06.

TABLE XV

Accuracy and precision of the combined extraction and [illegible] procedures for nickel, pyridine and thiocyanate.

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Component	Taken, mg (in H_2O)		Found *						D	Sx	E	Sx
			H_2O	Sx	$CHCl_3$	Sx	Total	Sx				
Nickel	27.38	mg	5.22	0.05	22.20	0.09	27.42	0.1[illegible]	[illegible]	0.05	[illegible]	0.2
		M x 10^3	0.977	0.009	4.30	0.02	-					
Pyridine	244.5	mg	9.12	0.08	-		-					
		M x 10^3	1.27	0.01	-		-					
Thiocyanate	1392	mg	1345	2	44.5	0.2	1390	?				
		M x 10^3	254.5	0.4	8.71	0.04	-					

* Mean of 5 extractions.

NOTES: (1) Equilibrium pH of aqueous phase was 6.72, Sx = 0.[illegible]

(2) Molar ratio of thiocyanate to nickel in chloroform phase was 2.03, Sx = 0.02.

phase could be determined by difference.

The analytical data from various other necessary extraction experiments are given in Table XVII. Remarks and conclusions concerning these results follow.

Extraction 1: In the absence of nickel, none of the reagents contained impurities that could be counted* as nickel.

Extraction 2: In the absence of pyridine, nickel was not measurably extracted in any form. Hence, the distribution ratios of nickel chloride** and nickel thiocyanate were extremely small.

Extraction 3: In the absence of thiocyanate, nickel was not measurably extracted in any form. Hence, the distribution ratio of nickel pyridine chloride could safely be ignored.

Extractions 4-6: These extractions, illustrated by Fig. 9, showed that the distribution ratio of nickel was inversely proportional to the temperature of the extraction system. It may readily be calculated, from Fig. 9, that the distribution ratio increased by 0.0003 per 0.1°C decrease in temperature. It was then evident that the extraction temperature would have to be controlled carefully in order to obtain reproducible results.

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* A 20-ml aliquot of either phase was taken for analysis. The colorimetric analysis (Appendix XIV) would detect as little as 0.1 µg of nickel in that aliquot (0.1 µg corresponds to an absorbance reading of 0.018). Since less than this amount of nickel was found, its concentration was less than 2.5×10^{-7} M.

** The metal was always added as a solution of the chloride salt (see Appendix IV).

TABLE XVI

Extractability of nickel into chloroform : Effect of reagents, temperature, shaking time and alcohol in chloroform on the distribution ratio (D) of the nickel

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : As indicated.
Extraction temperature : As indicated.

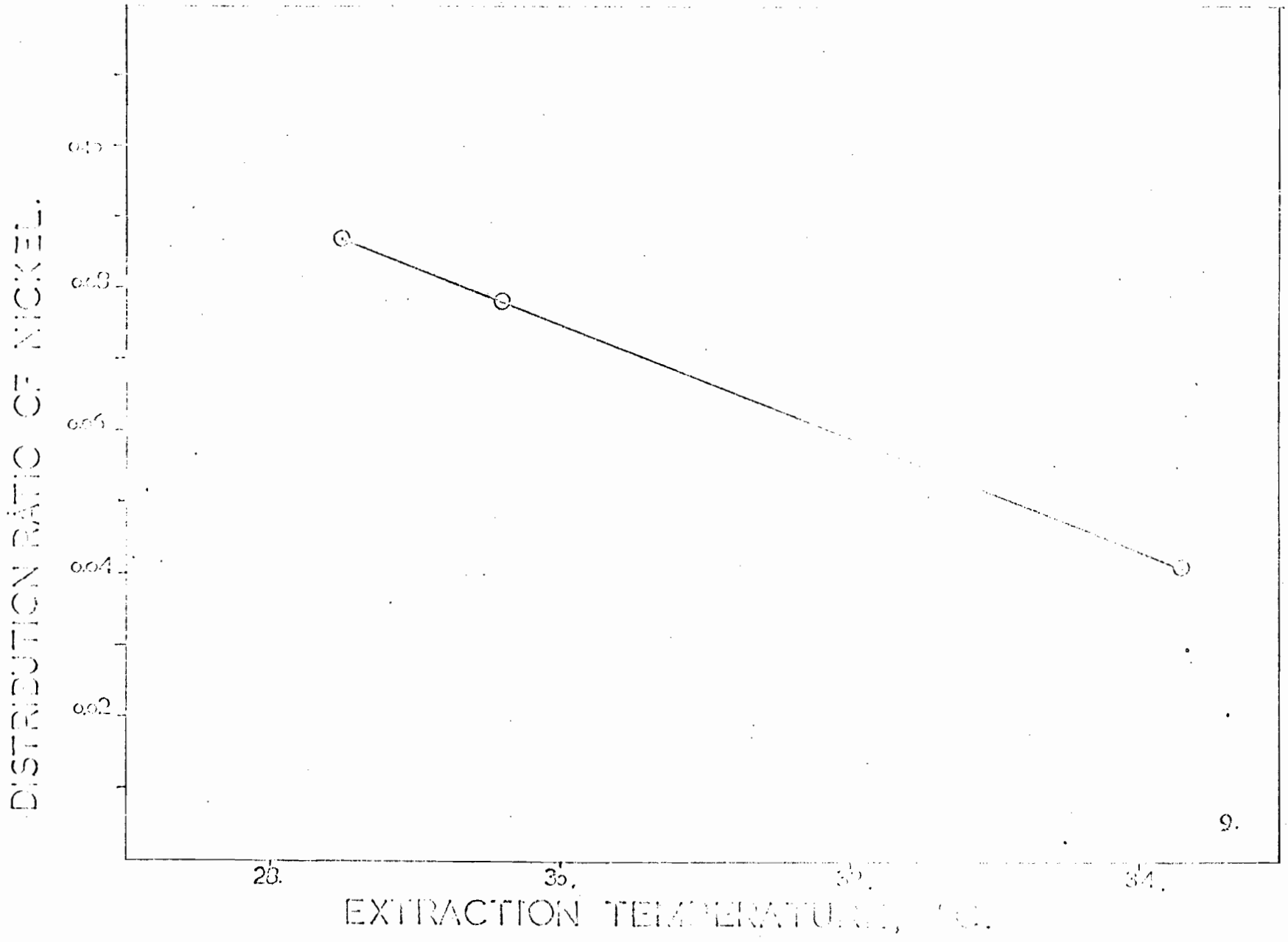
Ext. No.	Temp. (°C)	Mechanical shaking time (sec)	$CHCl_3$ grade	Nickel			Initial molar concentrations		
				Found, M x 10^2		D	Nickel	Pyridine	Thiocyanate
				H_2O	$CHCl_3$				
1	25.0	600	Reagent	0	0	--	0	0.3	0.3
2	"	"	"	--	0	0	0.0605	0	0.3
3	"	"	"	--	0	0	"	0.3	0
4	34.3	"	"	4.92 *	0.205	0.0417	"	0.03	0.3
5	29.6	"	"	4.76 *	0.342	0.0762	"	"	"
6	29.5	"	"	4.74 *	0.431	0.0959	"	"	"
7	25.0	30	"	4.49	0.677	0.154	"	"	"
8	"	40	"	4.40	0.673	0.153	"	"	"
9	"	70	"	4.42	0.683	0.155	"	"	"
10	"	120	"	4.44	0.679	0.153	"	"	"
11	"	600	"	4.39	0.673	0.153	"	"	"
12	"	1800	"	4.38	0.677	0.155	"	"	"
13	"	3600	"	4.38	0.660	0.151	"	"	"
14	"	600	Alcohol-free	4.39	0.668	0.152	"	"	"
15	"	600	Reagent	4.39	0.666	0.152	"	"	"

* Calculated by difference.

NOTE: See Appendix I for the preparation of alcohol-free chloroform.

FIGURE 9

Effect of temperature on the distribution ratio of nickel, as pyridine thiocyanate, in a chloroform-water extraction system.


DISTRIBUTION RATIO OF NICKEL
0.3
0.2
28.
EXTRACTION TEMPERATURE,

Extractions 7-13: These extractions* showed that equilibrium was attained very rapidly in systems of this kind. The chloroform was free from nickel before the extraction; yet in only 10 seconds of mechanical shaking, it had attained a constant concentration of nickel.

Extractions 14-15: Comparison of these extractions showed that the presence of ethanol in the chloroform (as a preservative) had no measurable effect on the distribution ratio of nickel.

3-2. Cobalt Pyridine and Picoline Thiocyanates

A set of replicate extractions was carried out, and the equilibrated phases analysed, for each of the cobalt pyridine, 2-picoline, 3-picoline and 4-picoline thiocyanate extraction systems. The results are in Tables XVII, XVIII, XIX and XX, respectively.

The analytical data from various other necessary extraction experiments on each of the above systems are given in Tables XXI, XXII, XXIII and XXIV, respectively. Remarks and conclusions concerning these experiments follow.

Extraction 1 (each Table): In the absence of cobalt, none of the reagents contained impurities that could be counted** as cobalt.

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* These extractions were carried out at room temperature (25 ± 3°C) but this temperature was constant. It is unlikely that the rate of equilibration would be much different at 25.0°C. In addition, it is certain that the use of 0.3-M thiocyanate in the aqueous phase (rather than 0.1-M) would increase the rate of equilibration.

** A 25-ml aliquot of either phase was taken for analysis. The colorimetric analysis (Appendix XIV) would detect as little as 0.5 μg of cobalt in that aliquot (0.5 μg corresponds to an absorbance reading of 0.002). Since less than this amount of cobalt was found, its concentration was less than 3.4×10^{-7} M.

TABLE XVII

Accuracy and precision of the combined extraction and the analytical procedures for cobalt, pyridine and thiocyanate

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Component	Taken, mg (in H_2O)		Found *						D	Sx	E	Sx
			H_2O	Sx	$CHCl_3$	Sx	Total	Sx				
Cobalt	13.84	mg	10.14	0.08	3.68	0.03	13.82	0.10	0.375	0.007	26.6	0.4
		M x 10^3	1.89	0.02	0.709	0.006	-					
Pyridine	294.3	mg	19.3	0.3	-		-					
		M x 10^3	2.68	0.04	-		-					
Thiocyanate	1429	mg	-		7.49	0.12	-					
		M x 10^3	-		1.46	0.03	-					

* Mean of 4 extractions.

NOTES: (1) Equilibrium pH of aqueous phase was 6.97, Sx = 0.05.

(2) Molar ratio of thiocyanate to cobalt in chloroform phase was 2.03, Sx = 0.04.

TABLE XVIII

Accuracy and precision of the combined extraction and the analytical procedures for cobalt and 2-picoline (thiocyanate not determined)

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Component	Taken, mg (in H_2O)		Found *						D	Sx	E	Sx
			H_2O	Sx	$CHCl_3$	Sx	Total	Sx				
Cobalt	13.84	mg	12.73	0.08	1.05	0.02	13.78	0.09	0.0797	0.0020	7.63	0.19
		M x 10^3	2.46	0.02	0.196	0.004	-					
2-Picoline	3261	mg	76.8	0.8	-		-					
		M x 10^3	9.39	0.10	-		-					
Thiocyanate	1387	mg	-		-		-					
		M x 10^3	-		-		-					

* Mean of 4 extractions.

NOTE: Equilibrium pH of aqueous phase was 8.03, Sx = 0.05.

TABLE XIX

Accuracy and precision of the combined extraction and the analytical procedures for cobalt, 3-picoline and thiocyanate

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Component	Taken, mg (in H_2O)	Found *						D	Sx	E	Sx
			H_2O	Sx	$CHCl_3$	Sx	Total	Sx				
Cobalt	13.80	mg	5.51	0.05	8.22	0.05	13.73	0.07	1.53	0.03	60.0	0.4
		M x 10^3	1.03	0.01	1.58	0.01	-					
3-Picoline	475	mg	7.73	0.07	-		-					
		M x 10^3	0.914	0.008	-		-					
Thiocyanate	1387	mg	-		16.8	0.1	-					
		M x 10^3	-		3.27	0.02	-					

* Mean of 4 extractions.

NOTES: (1) Equilibrium pH of aqueous phase was 6.72, Sx = 0.11.

(2) Molar ratio of thiocyanate to cobalt in chloroform phase was 2.07, Sx = 0.03.

TABLE XX

Accuracy and precision of the combined extraction and the analytical procedures for cobalt, 4-picoline and thiocyanate

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Component	Taken, mg (in H_2O)	Found *						D	Sx	E	Sx
			H_2O	Sx	$CHCl_3$	Sx	Total	Sx				
Cobalt	13.84	mg	5.49	0.05	8.24	0.05	13.73	0.08	1.56	0.02	60.3	0.3
		M x 10^3	1.02	0.01	1.59	0.01	-					
4-Picoline	284.6	mg	5.24	0.11	-		-					
		M x 10^3	0.619	0.013	-		-					
Thiocyanate	1391	mg	-		16.5	0.1	-					
		M x 10^3	-		3.23	0.02	-					

* Mean of 4 extractions.

NOTES: (1) Equilibrium pH of aqueous phase was 6.74, Sx = 0.02.

(2) Molar ratio of thiocyanate to cobalt in chloroform phase was 2.03, Sx = 0.03.

TABLE XXI

Extraction of cobalt into chloroform : Effect of reagents, temperature, shaking time, and alcohol in chloroform on the distribution ratio (D) of the metal

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : As indicated.
Extraction temperature : As indicated.

Ext. No.	Temp. (°C)	Mechanical shaking time (sec)	$CHCl_3$ grade	Cobalt			Initial molar concentrations		
				Found, M x 10^3		D	Cobalt	Pyridine	Thiocyanate
				H_2O	$CHCl_3$				
1	25.0	600	Reagent	0	0	-	0	0.110	0.2894
2	"	"	"	-	0	0	0.00246	0	"
3	"	"	"	-	0	0	"	0.110	0
4	21.0	"	"	0.331	2.16	6.53	"	0.0817	0.2894
5	33.5	"	"	1.09	1.39	1.27	"	"	"
6	25.0	10	"	0.462	2.03	4.40	"	"	"
7	"	600	"	0.444	2.05	4.62	"	"	"
8	"	1800	"	0.444	2.05	4.62	"	"	"
9	"	600	Alcohol-free	0.443	2.04	4.61	"	"	"
10	"	600	"	0.450	2.03	4.51	"	"	"

NOTE : See Appendix I for the preparation of alcohol-free chloroform.

TABLE XXII

Extraction of cobalt into chloroform : Effect of reagents, shaking time, and alcohol in chloroform on the distribution ratio (D) of the metal

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : As indicated.
Extraction temperature : 25.0°C.

Ext. No.	Mechanical shaking time (sec)	$CHCl_3$ grade	Cobalt			Initial molar concentrations		
			Found, M x 10^3		D	Cobalt	2-Picoline	Thiocyanate
			H_2O	$CHCl_3$				
1	600	Reagent	0	0	-	0	0.385	0.2653
2	"	"	-	0	0	0.00258	0	"
3	"	"	-	0	0	"	0.385	0
4	"	"	2.48	0.198	0.0798	"	"	0.2653
5	1800	"	2.46	0.200	0.0813	"	"	"
6	3600	"	2.47	0.194	0.0785	"	"	"
7	7200	"	2.49	0.204	0.0819	"	"	"
8	600	Alcohol-free	2.48	0.203	0.0819	"	"	"
9	600	"	2.48	0.201	0.0810	"	"	"

NOTE: See Appendix I for the preparation of alcohol-free chloroform.

TABLE XXIII

Extraction of cobalt into chloroform : Effect of reagents, shaking time, alcohol in chloroform, and thiocyanate concentration on the distribution ratio (D) of the metal

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : As indicated.
Extraction temperature : 25.0°C.

Ext. No.	Mechanical shaking time (sec)	$CHCl_3$ grade	Cobalt			Initial molar concentrations		
			Found, M x 10^3		D	Cobalt	3-Picoline	Thiocyanate
			H_2O	$CHCl_3$				
1	600	Reagent	0	0	-	0	0.0567	0.2653
2	"	"	-	0	0	0.00260	0	"
3	"	"	-	0	0	"	0.0567	0
4	"	"	1.02	1.57	1.54	"	"	0.2653
5	1800	"	1.03	1.59	1.55	"	"	"
6	3600	"	1.02	1.57	1.54	"	"	"
7	7200	"	1.03	1.59	1.54	"	"	"
8	600	Alcohol-free	1.03	1.58	1.54	"	"	"
9	600	Reagent	1.04	1.58	1.52	"	"	0.2547

NOTE: See Appendix I for the preparation of alcohol-free chloroform.

TABLE XXIV

Extraction of cobalt into chloroform : Effect of reagents, shaking time, alcohol in chloroform, and thiocyanate concentration on the distribution ratio (D) of the metal

Initial volume of each phase : 90 ml.
Final phase volume : See Table IV.
Mechanical shaking time : As indicated.
Extraction temperature : 25.0°C.

Ext. No.	Mechanical shaking time (sec)	$CHCl_3$ grade	Cobalt			Initial molar concentrations		
			Found, M x 10^3		D	Cobalt	4-Picoline	Thiocyanate
			H_2O	$CHCl_3$				
1	600	Reagent	0	0	-	0	0.0340	0.2660
2	"	"	-	0	0	0.00258	0	"
3	"	"	-	0	0	"	0.0340	0
4	"	"	1.02	1.58	1.55	"	"	0.2660
5	1800	"	1.02	1.59	1.56	"	"	"
6	3600	"	1.02	1.58	1.55	"	"	"
7	7200	"	1.03	1.58	1.54	"	"	"
8	600	Alcohol-free	1.03	1.59	1.55	"	"	"
9	600	Reagent	1.03	1.58	1.54	"	"	0.2553

NOTE: See Appendix I for the preparation of alcohol-free chloroform.

Extraction 2 (each Table): In the absence of pyridine (or picoline), cobalt was not measurably extracted in any form. Hence, the distribution ratios of cobalt chloride** and cobalt thiocyanate were extremely small.

Extraction 3 (each Table): In the absence of thiocyanate, cobalt was not measurably extracted in any form. Hence, the distribution ratios of cobalt pyridine (and picoline) chlorides could safely be ignored.

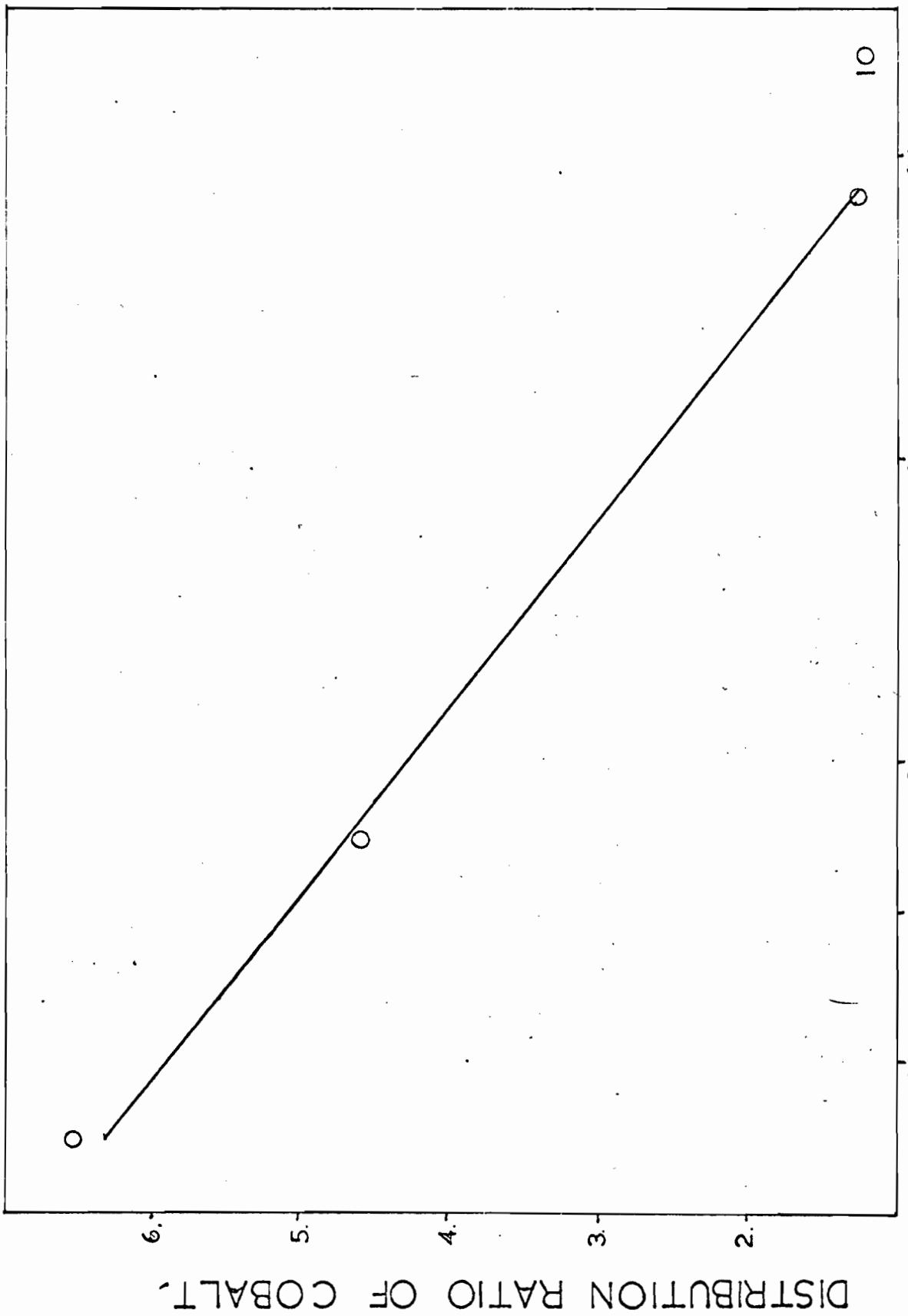
Extractions 4, 5 and 7 (Table XXI): These extractions, illustrated by Fig. 10, showed that the distribution ratio of cobalt pyridine thiocyanate was inversely proportional to the temperature of the extraction system. It may readily be calculated from Fig. 10 that the distribution ratio increases by 0.032 per 0.1°C decrease in temperature. It was then evident that the extraction temperature would have to be controlled carefully in order to obtain reproducible results.

Extractions 6-8 (Table XXI); Extractions 4-7 (Table XXII); Extractions 4-7 (Table XXIII); Extractions 4-7 (Table XXIV): These extractions showed that equilibrium was attained very rapdily in cobalt pyridine (and picoline) thiocyanate extractions systems. The chloroform was free from cobalt before the extraction, yet in 10 minutes (or less) of mechanical shaking, it had attained a constant concentration of cobalt.

** The metal was always added as a solution of the chloride salt (see Appendix IV).

FIGURE 10

Effect of temperature on the distribution ratio of cobalt, as pyridine thiocyanate, in a chloroform-water extraction system.


DISTRIBUTION RATIO OF COBALT.
6.
5.
4.
3.
2.
22.
26.
30.
34.
EXTRACTION TEMPERATURE, °C.
10

Extractions 7, 9 and 10 (Table XXI); Extractions 4, 8 and 9 (Table XXII); Extractions 4 and 8 (Table XXIII); Extractions 4 and 8 (Table XXIV): A comparison of these extractions, in each table, showed that the presence of ethanol in the chloroform (as a preservative) had no measurable effect on the distribution ratios of cobalt pyridine and picoline thiocyanates.

Extractions 4 and 9 (Tables XXIII and XXIV): A comparison of these extractions, in each table, showed that a small decrease in the thiocyanate concentration of the aqueous phase had no measurable effect on the distribution ratios of cobalt 3-picoline and 4-picoline thiocyanates.

3-3. Zinc and Cadmium Pyridine Thiocyanates

A set of replicate extractions was carried out, and the equilibrated phases analysed, for these extraction systems. The results are given in Tables XXV and XXVI, respectively.

The analytical data from various other necessary extraction experiments are given in Tables XXVII and XXVIII, respectively. Remarks and conclusions concerning these experiments follow.

Extraction 1 (each Table): In the absence of zinc or cadmium, none of the reagents contained impurities that could be counted* as either

* A 50-ml aliquot of either phase was taken. Less than 0.02 ml of 0.01-M ethylenediaminetetraacetic acid was required to complete the titration (see Appendix XV for details). Therefore the concentrations of zinc and cadmium together were less than 4×10^{-6} M.

TABLE XXV

Accuracy and precision of the combined extraction and the analytical procedures for zinc, pyridine and thiocyanate

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Component	Taken, mg (in H_2O)		Found*						D	S_x	E	S_x
			H_2O	S_x	$CHCl_3$	S_x	Total	S_x				
Zinc	30.39	mg	1.02	0.02	29.33	0.03	30.35	0.09				
		M x 10^3	0.172	0.004	5.06	0.02	-		29.4	0.7	96.7	0.1
Pyridine	809.6	mg	48.5	0.7	-		-					
		M x 10^3	6.79	0.10	-		-					
Thiocyanate	1389	mg	-		52.3	0.3	-					
		M x 10^3	-		10.15	0.06	-					

* Mean of 4 extractions.

NOTES: (1) Equilibrium pH of aqueous phase was 6.96, S_x = 0.03.

(2) Molar ratio of thiocyanate to zinc in chloroform phase was 2.01, S_x = 0.02.

TABLE XXVI

Accuracy and precision of the combined extraction and the analytical procedures for cadmium, pyridine and thiocyanate

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Component	Taken, mg (in H_2O)		Found*						D	S_x	E	S_x
			H_2O	S_x	$CHCl_3$	S_x	Total	S_x				
Cadmium	12.86	mg	5.34	0.04	7.56	0.06	12.90	0.04				
		M x 10^3	0.524	0.004	0.761	0.006	-		1.45	0.01	58.6	0.3
Pyridine	591.7	mg	37.7	0.3	-		-					
		M x 10^3	5.26	0.04	-		-					
Thiocyanate	1389	mg	-		8.02	0.09	-					
		M x 10^3	-		1.56	0.02	-					

* Mean of 4 extractions.

NOTES : (1) Equilibrium pH of aqueous phase was 7.30, S_x = 0.03.

(2) Molar ratio of thiocyanate to cadmium in chloroform phase was 2.05, S_x = 0.04.

TABLE XXVII

Extraction of zinc into chloroform : Effect of reagents, shaking time, and alcohol in chloroform on the distribution ratio (D) of the metal

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : As indicated.
Extraction temperature : 25.0°C.

Ext. No.	Mechanical shaking time (sec)	$CHCl_3$ grade	Zinc			Initial molar concentrations		
			Found, M x 10^3		D	Zinc	Pyridine	Thiocyanate
			H_2O	$CHCl_3$				
1	600	Reagent	0	0	-	0	0.1137	0.2657
2	"	"	-	0	0	0.00513	0	"
3	"	"	-	0	0	"	0.1137	0
4	120	"	0.172	5.07	29.5	"	"	0.2657
5	600	"	0.170	5.04	29.7	"	"	"
6	1800	"	0.178	5.06	28.4	"	"	"
7	3600	"	0.170	5.06	29.7	"	"	"
8	600	Alcohol-free	2.687	2.513	0.937	"	0.0223	"
9	"	"	2.684	2.508	0.934	"	"	"
10	"	Reagent	2.677	2.514	0.939	"	"	"
11	"	"	2.679	2.514	0.938	"	"	"

NOTE: See Appendix I for the preparation of alcohol-free chloroform.

TABLE XXVIII

Extraction of cadmium into chloroform : Effect of reagents, shaking time, and alcohol in chloroform on the distribution ratio (D) of the metal

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time: As indicated.
Extraction temperature : 25.0°C.

Ext. No.	Mechanical shaking time (sec)	$CHCl_3$ grade	Cadmium			Initial molar concentrations		
			Found, M x 10^3		D	Cadmium	Pyridine	Thiocyanate
			H_2O	$CHCl_3$				
1	600	Reagent	0	0	-	0	0.0831	0.2657
2	"	"	-	0	0	0.001270	0	"
3	"	"	-	0	0	"	0.0831	0
4	120	"	0.531	0.760	1.43	"	"	0.2657
5	600	"	0.528	0.769	1.46	"	"	"
6	1800	"	0.526	0.764	1.45	"	"	"
7	3600	"	0.531	0.759	1.43	"	"	"
8	600	Alcohol-free	0.524	0.761	1.45	"	"	"

NOTE: See Appendix I for the preparation of alcohol-free chloroform.

zinc or cadmium.

Extraction 2 (each Table): In the absence of pyridine, neither zinc nor cadmium was measurably extracted in any form. Therefore, the distribution ratios of zinc chloride*, zinc thiocyanate, cadmium chloride* and cadmium thiocyanate were extremely small.

Extraction 3 (each Table): In the absence of thiocyanate, neither zinc nor cadmium was measurably extracted. Therefore, the distribution ratios of zinc and cadmium pyridine chlorides could safely be ignored.

Extractions 4-7 (each Table): These extractions showed that equilibrium was attained very rapidly in zinc and cadmium pyridine thiocyanate extraction systems. The chloroform was free from either zinc or cadmium before the extraction, yet in 2 minutes (or less) of mechanical shaking, it had attained a constant concentration of metal.

Extractions 8-11 (Table XXVII); Extractions 5 and 8 (Table XXVIII): A comparison of these extractions, in each table, showed that the presence of ethanol in the chloroform (as a preservative) had no measurable effect on the distribution ratios of zinc and cadmium pyridine thiocyanates.

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* The metal was always added as a solution of the chloride salt (see Appendix IV).

3-4. Summary and Conclusions

In the absence of any added metal, none of the extraction systems contained impurities that could be counted as the metal under investigation.

Experimental data are reported in Part V-4 for extractions carried out in the absence of pyridine (or picoline). One, or both phases of these extraction systems were titrated for pyridine; no impurities were present which could be counted as pyridine (see Table XXIX, for example).

When pyridine (or picoline) was absent from an extraction system, none of the metals was measurably extracted into chloroform. Therefore, the distribution ratios of the metal chlorides and the metal thiocyanates were negligibly small in the presence of 0.3-M potassium thiocyanate. In Part V-4, extractions are reported in which pyridinium (or picolinium) chloride was present. However, when pyridine (or picoline) was absent from those systems, none of the metals was measurably extracted into chloroform. Therefore, the distribution ratios of the metal pyridinium (or picolinium) chlorides or thiocyanates* were also negligibly small.

When thiocyanate was absent from an extraction system, none of the metals was measurably extracted in the presence of pyridine. Similarly, cobalt was not measurably extracted in the presence of any picoline. Therefore, the distribution ratios of metal pyridine chlorides and of cobalt

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* These complexes may be represented by $(PH^+)_y$ (MX^{y-}_{y+2}) where M = divalent metal, PH^+ = pyridinium or picolinium ion, and X = thiocyanate or chloride ion.

picoline chlorides were negligibly small. It was assumed that the distribution ratios of nickel, zinc and cadmium picoline chlorides could also be safely neglected.

The careful control of the extraction temperature has been shown to be important for cobalt and nickel pyridine thiocyanate extraction systems. It was expected that the other systems chosen for study would also be temperature dependent. All extractions reported in this section were carried out at constant temperature, and all extractions reported in Part V-4 were carried out at 25.0 ± 0.05°C.

Equilibrium has been shown to be established within a 10-minute shaking period, for each of the metal pyridine thiocyanate extraction systems and for each of the cobalt picoline thiocyanate systems. It was expected that equilibrium would be reached during this shaking period in each of the nickel, zinc and cadmium picoline thiocyanate extraction systems.

A small decrease (about 4 percent) in the initial thiocyanate concentration of the aqueous phase has been shown to have no measurable effect on the distribution ratio of cobalt 3-picoline (or 4-picoline) thiocyanate at the low concentration level employed for the metal. These experiments supported the assumption that extractions carried out from a medium of nearly constant ionic strength could be inter-compared. Of course the thiocyanate concentration of the aqueous phase was decreased slightly due to the metal pyridine (or picoline) thiocyanate complex being extracted into the chloroform*.

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* The maximum metal concentration used was 0.005M (see Part V-2). Therefore, if the initial thiocyanate concentration was 0.3M, and all the metal was extracted, then the decrease in the thiocyanate concentration would be 0.01M (i.e. a 3.3 percent decrease). The effect of variations in the thiocyanate concentration of the aqueous phase on the distribution ratio of each metal is considered in detail in Appendix XVIIIC.

The presence of alcohol in the chloroform reagent had no effect on the distribution ratios of metal for any of the metal pyridine thiocyanate extraction systems or on any of the cobalt picoline thiocyanate systems.

The replicate extractions carried out for each of the metal pyridine thiocyanate systems and for each of the cobalt picoline thiocyanate systems showed that the molar ratio of thiocyanate to metal in the chloroform phase was twice unity. Further evidence of this fact is shown in Part V-4. Clearly, only the di-thiocyanate of the various metal pyridine (and picoline) complexes was present in the chloroform phase. This ratio was also found when the aqueous phase contained picolinium chloride (see Table L). This evidence supported the results in Part V-1 which described the small distribution ratios of various chlorides and thiocyanates.

4. Final Extraction Data

In the present Section, equilibrium data are presented for the selected metal pyridine (and picoline) thiocyanate extraction systems. The percent metal extracted* (E) and the distribution ratio of the metal** (D) are plotted against the total equilibrium concentration of pyridine or

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* The plots of E against $[P]_{T,A}$ were always made on linear scales.

** In the extraction systems, D was found to vary from nil to a value of several hundred over the range of $[P]_{T,A}$ that was used. For this reason, D was not plotted on a linear $[P]_{T,A}$ scale, but on a combination of a linear scale (small values of D) and a logarithmic scale (higher values of D). This method allowed the data to be presented more accurately and more usefully. In addition, the overall shape of the distribution curve could be seen.

picoline in the aqueous phase, $[P]_{T,A}$.

In the general expression relating D to $[P]$ (see Part I-1, equations (13) and (17)), $[P]$ represents the equilibrium concentration of free (uncomplexed) pyridine (or picoline) in the aqueous phase. However, it was the total pyridine or picoline (free plus complexed) that was measured. In making theoretical use of the analytical data later, the concentration of free pyridine (or picoline) was calculated for each system. However, for the present graphical presentations, it was considered satisfactory to plot E and D against the total equilibrium concentration of pyridine (or picoline) in the aqueous phase, $[P]_{T,A}$.

The extractions reported here (Part V-4) were carried out at 25.0 ± 0.05°C. A summary of the actual extraction and the analytical procedures is given in Part V-1.

The nickel pyridine thiocyanate system is reported first; it was studied in more detail than the others. In particular, the effect of varying the initial concentration of nickel was found to give anomalous results*. In an effort to explain these results, the effect of the following factors on extraction was studied: (1) the pH of the aqueous phase; (2) the presence of carbon dioxide dissolved in both phases; and (3) the nature of the organic solvent itself, by comparing chloroform with benzene.

4-1. Nickel Pyridine Thiocyanate

(a) Effect of the Initial Concentration of Nickel on the Distribution Ratio

The distribution of nickel pyridine thiocyanate between chloroform

* A similar study of the metal concentration was also undertaken on cobalt.

and aqueous solutions of 0.3-M thiocyanate was studied as a function of the equilibrium concentration of pyridine. Three different, initial concentrations of nickel were used. These were 0.005M, 0.0025M, and 0.0005M. The results are given in Tables XXIX, XXX and XXXI, respectively. The plots of E and D against the total equilibrium concentration of pyridine in the aqueous phase are in Figs. 11A and 11B.

It is seen that the distribution curves were progressively displaced to the left as smaller initial concentrations of nickel were used in the system. An explanation was sought for these displacements.

Dimerization (or polymerization) of the complex in the chloroform phase would not explain these displacements. In equation (13)*, the dimerization constant (K_D) appears in the numerator. Therefore, dimerization would cause the distribution ratio of nickel to increase, at a given concentration of pyridine, as the concentration of nickel in the extraction system is increased. This was not the case.

In Figs. 11A and 11B the free pyridine concentration strictly should be plotted, rather than the total (free plus complexed) pyridine concentration**. In order to determine whether or not plots of the free pyridine concentration would eliminate the displacements, calculations of the concentrations of bound pyridine in the aqueous phase were made by using the available stability-constant data (57). In an aqueous solution 5×10^{-3} M in nickel, 0.3M in thiocyanate and 5×10^{-4} M in pyridine, it was calculated that only two percent of the total pyridine was complexed

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* See Part I-2.

** The analysis of the aqueous phase for pyridine, gave total pyridine. See Part IV-1 for details.

TABLE XXIX A

Effect of the pyridine concentration on the distribution of nickel between chloroform and aqueous thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Nickel				Pyridine				Thiocyanate				Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	$CHCl_3$	Total	Taken, mg (in H_2O)	Found, mg H_2O	$CHCl_3$	Total	Taken, mg (in H_2O)	Found, mg H_2O	$CHCl_3$	Total	
1	27.38	27.41	0	27.41	0	0	0	0	1392	1385	0	1385	6.01
2	"	27.50	0.0074	27.51	8.15	1.35	7.30	8.45	"	1384	0	1384	6.20
3	"	26.66	0.742	27.40	40.8	3.38	38.6	42.0	"	1383	1.66	1385	6.44
4	"	23.22	4.22	27.44	81.5	5.16	74.0	79.2	"	1377	8.80	1385	6.47
5	"	18.56	8.73	27.29	122.2	6.26	116	122	"	1368	17.9	1386	6.54
6	"	13.86	13.78	27.64	163.0	6.86	156	163	"	1358	27.5	1386	6.57
7	"	8.74	18.35	27.09	203.8	7.79	196	204	"	1348	36.6	1385	6.65
8R	"	5.22	22.20	27.42	244.5	9.12	-	-	"	1345	44.5	1390	6.72
9	"	2.76	24.51	27.27	285.2	11.3	-	-	"	-	49.4	-	6.79
10	"	1.41	25.92	27.33	326.0	13.1	-	-	"	-	52.5	-	6.80
11	"	0.740	26.63	27.37	366.6	16.1	348	364	"	1338	53.7	1392	6.82
12	"	0.252	27.06	27.31	448.3	19.3	433	452	"	1335	54.4	1389	6.87
13	"	0.0521	27.41	27.46	815	43.2	779	822	"	1327	54.9	1392	7.08

NOTE: Extraction 8R is the mean of 5 replicates.

TABLE XXIX B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for nickel pyridine thiocyanate extractions*

Ext. No.	Nickel				Pyridine		Thiocyanate		Molar ratio of thiocyanate to nickel in $CHCl_3$ phase
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$	Found, M x 10^3 H_2O	$CHCl_3$	
1	5.12	0	0	0	0	0	261.3	0	-
2	5.14	0.00143	0.000278	0.027	0.187	1.05	261.1	0	0
3	4.98	0.143	0.0287	2.69	0.469	5.55	260.9	0.325	2.27
4	4.34	0.818	0.188	15.3	0.716	10.6	259.8	1.72	2.10
5	3.47	1.71	0.493	32.2	0.870	16.7	258.4	3.50	2.05
6	2.59	2.70	1.04	50.2	0.953	22.4	257.0	5.38	1.99
7	1.64	3.59	2.19	68.0	1.08	28.1	255.0	7.16	2.00
8R	0.977	4.30	4.40	81.1	1.27	34.0**	254.5	8.71	2.03
9	0.518	4.78	9.23	90.0	1.58	39.3**	254.3**	9.65	2.02
10	0.264	5.06	19.2	95.1	1.82	45.0**	253.7**	10.2	2.02
11	0.139	5.20	37.4	97.4	2.24	49.9	253.5	10.5	2.02
12	0.0474	5.27	111	99.1	2.69	62.0	253.3	10.6	2.01
13	0.00983	5.32	542	99.8	6.04	111	253.0	10.7	2.01

* Basic data are in Table XXIX A.

** Calculated by difference.

TABLE XXX A

Effect of the pyridine concentration on the distribution of nickel between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Nickel				Pyridine		Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Total	Taken, mg (in H_2O)	Found, mg H_2O	
1	13.69	13.14	0.478	13.62	40.8	3.19	6.42
2	"	11.98	1.531	13.51	61.1	4.47	6.70
3	"	10.55	3.06	13.61	81.5	5.10	6.63
4	"	6.86	6.58	13.44	122.2	6.62	6.68
5	"	3.90	9.62	13.52	163.0	8.22	6.77
6	"	1.84	11.46	13.30	203.8	10.0	6.83
7	"	0.870	12.63	13.50	244.5	12.2	6.83
8	"	0.229	13.40	13.63	326.0	16.9	6.92

* 1392 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE XXX B

Distribution ratio (D), percent extraction (E), and molar concentrations (M) for nickel pyridine thiocyanate extractions*

Ext. No.	Nickel				Pyridine		Thiocyanate***	
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O	$CHCl_3$
1	2.46	0.0927	0.0377	3.51	0.442	5.56	262.7	0.195
2	2.24	0.297	0.133	11.4	0.620	8.15	262.3	0.594
3	1.97	0.594	0.302	22.6	0.707	10.1	261.6	1.19
4	1.28	1.27	0.993	49.1	0.919	16.6	260.3	2.54
5	0.729	1.86	2.55	71.2	1.14	22.3	259.6	3.72
6	0.345	2.22	6.44	86.2	1.40	27.9	258.8	4.44
7	0.163	2.44	15.0	93.5	1.70	33.3	258.7	4.88
8	0.0430	2.59	60.2	98.4	2.35	44.3	258.7	5.18

* Basic data are in Table XXX A.

** Calculated by difference.

*** The molar ratio of thiocyanate to nickel in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known nickel concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

TABLE XXXI A

Effect of the pyridine concentration on the distribution of nickel between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Nickel				Pyridine		Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O	
1	2.738	2.580	0.115	2.695	40.8	3.15	6.50
2	"	2.290	0.452	2.742	61.1	4.35	6.73
3	"	1.705	1.026	2.731	81.5	5.53	6.74
4	"	1.243	1.485	2.728	101.8	6.87	6.94
5	"	0.746	1.981	2.727	122.2	8.03	6.77
6	"	0.296	2.458	2.754	163.0	10.12	6.83
7	"	0.0574	2.668	2.725	244.5	15.32	6.80
8	"	0.0318	2.723	2.755	285.2	18.18	6.82
9	"	0.0220	2.720	2.742	326.0	20.78	6.92
10	"	0.01308	2.730	2.743	366.6	22.96	6.92
11	"	0.00828	2.742	2.750	448.3	29.43	7.00

* 1392 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE XXXI B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for nickel pyridine thiocyanate extractions*

Ext. No.	Nickel				Pyridine		Thiocyanate***	
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O	$CHCl_3$
1	0.482	0.0223	0.0463	4.28	0.437	5.57	262.8	0.0446
2	0.428	0.0877	0.205	16.5	0.603	8.17	262.6	0.175
3	0.318	0.199	0.626	37.7	0.767	10.9	262.5	0.398
4	0.232	0.288	1.24	54.5	0.954	13.7	262.5	0.576
5	0.140	0.384	2.74	72.8	1.11	16.4	262.3	0.768
6	0.0552	0.478	8.66	89.4	1.40	22.0	262.1	0.956
7	0.0107	0.516	48.2	97.9	2.13	32.9	262.0	1.03
8	0.00596	0.527	88.4	98.9	2.52	38.4	262.5	1.05
9	0.00413	0.525	127	99.2	2.89	43.8	262.5	1.05
10	0.00245	0.528	215	99.5	3.20	49.2	263.0	1.06
11	0.00155	0.530	342	99.7	4.19	60.0	263.2	1.06

* Basic data are in Table XXXI A.

** Calculated by difference.

*** The molar ratio of thiocyanate to nickel in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known nickel concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

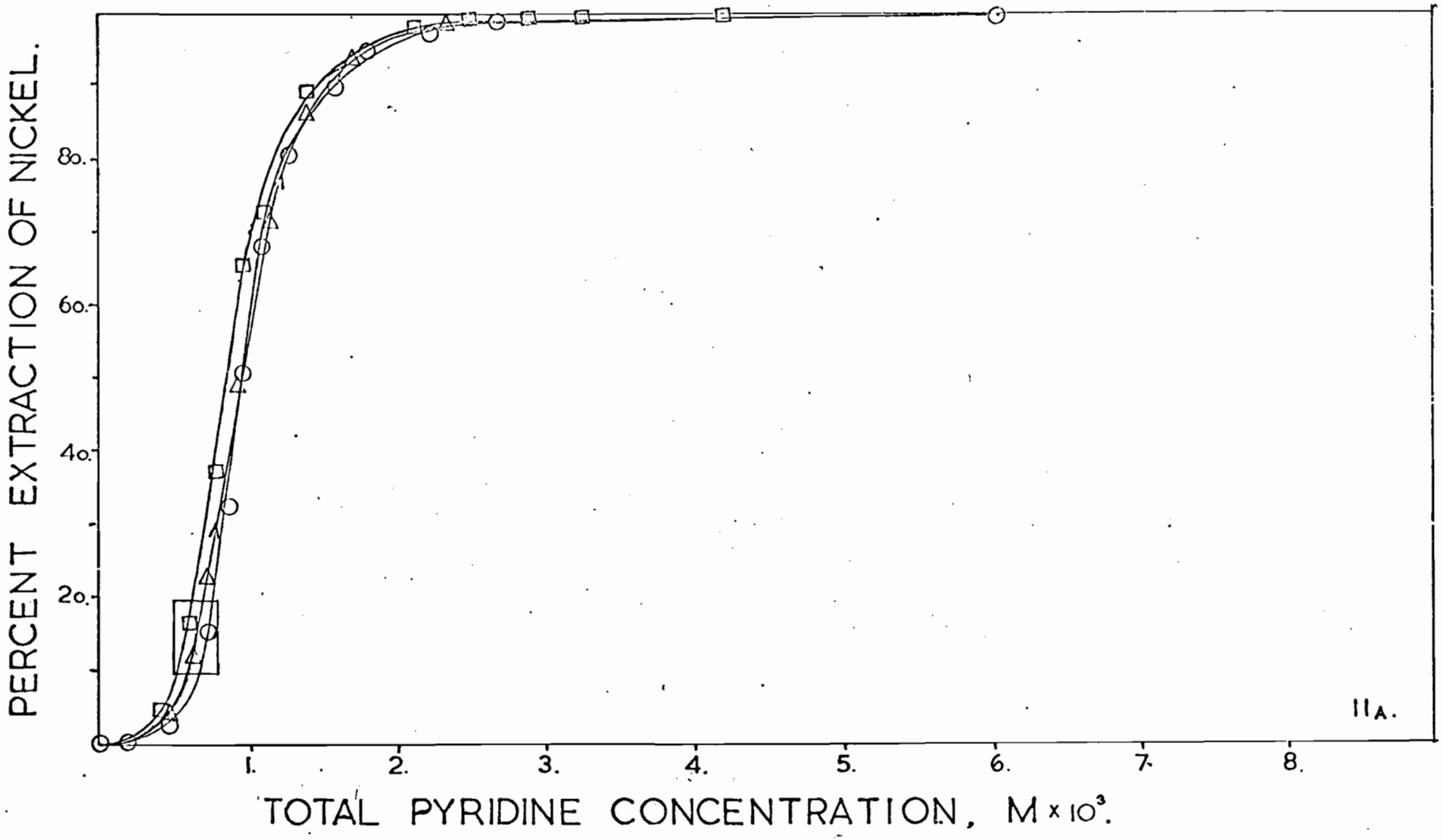
FIGURES 11A AND 11B

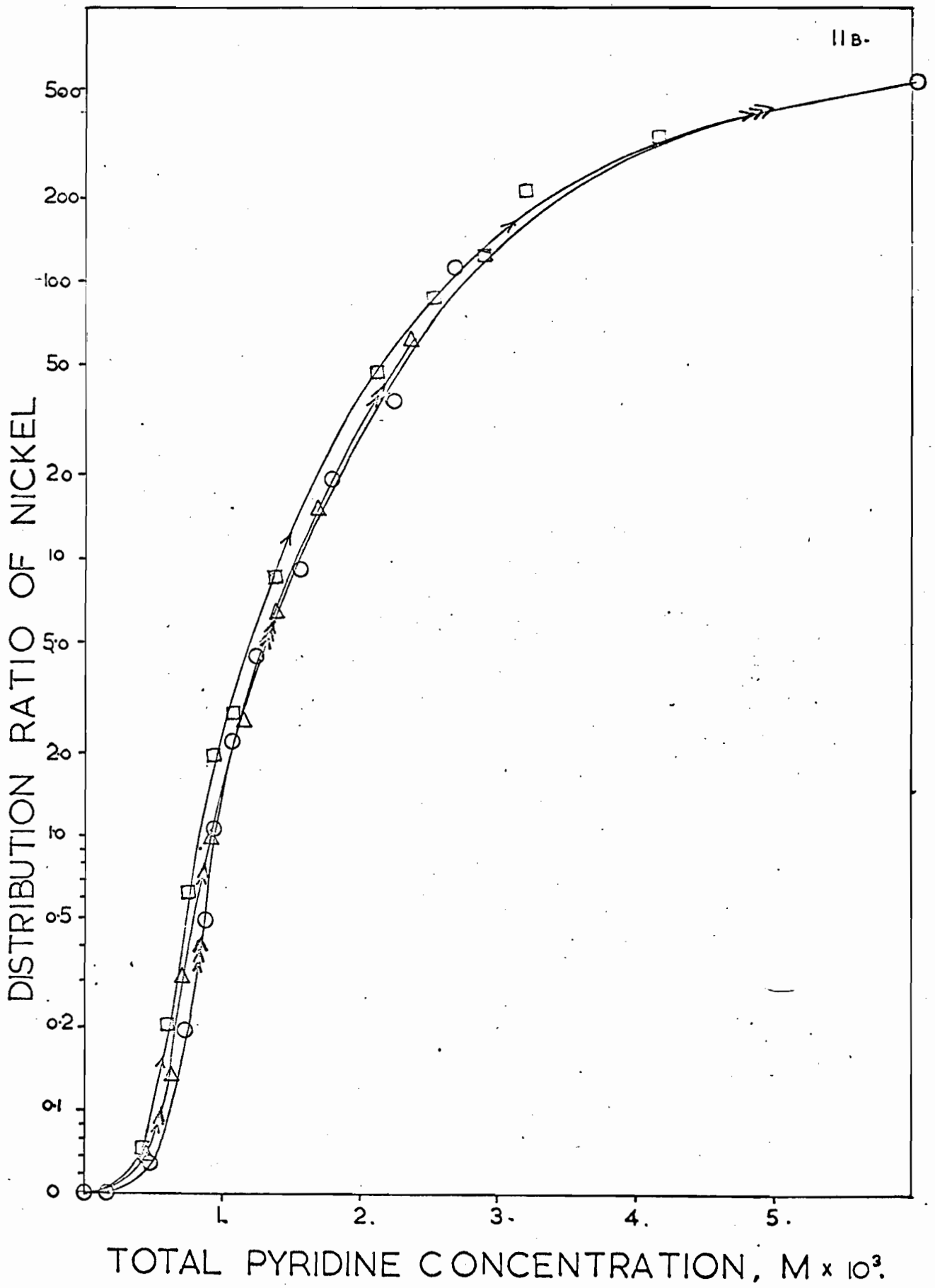
Extraction of nickel pyridine thiocyanate into chloroform, as a function of the total equilibrium concentration of pyridine in the aqueous phase; effect of different, initial concentrations of nickel on the percent extraction (11A) and on the distribution ratio (11B).

$\odot$ = 5×10^{-3}-M nickel (initial).

$\triangle$ = 2.5×10^{-3}-M nickel (initial).

$\boxdot$ = 5×10^{-4}-M nickel (initial).


PERCENT EXTRACTION OF NICKEL.
80.
60.
40.
20.
1.
2.
3.
4.
5.
6.
7.
8.
TOTAL PYRIDINE CONCENTRATION, M x 10³.
11A.


11B.
DISTRIBUTION RATIO OF NICKEL
500
200
100
50
20
10
5·0
2·0
1·0
0·5
0·2
0·1
0
1.
2.
3.
4.
5.
TOTAL PYRIDINE CONCENTRATION, M x 10³.

as Ni P_x^{++} (where x = 1,2,3). Such a solution is similar to the aqueous phase of extraction 4 in Table XXIX, which was in a region of the distribution curve where the displacements were especially noticeable. It was concluded that complexation of pyridine in the aqueous phase could not explain the observed curve displacements.

A variable extraction error was next considered. In the extraction procedure (see Appendix IV), the phases of the extraction system were allowed to separate in a separatory funnel. Here, small droplets of chloroform were occluded to the side of the funnel above the liquid level, and on the surface of the lighter aqueous phase. If these droplets evaporated to some extent, then the less volatile pyridine would have been released into the chloroform phase and counted as part of the equilibrium pyridine concentration of that phase. In order to test whether or not the above occurred, it was assumed that the amount of pyridine released was proportional to the standing time. Four replicate extractions (each similar to extraction 5 in Table XXIX) were carried out. Each aqueous phase was analysed for pyridine (found, mg; 5.76, S_x = 0.11). Each aqueous phase was re-analysed for pyridine after 20 hours (found, mg; 5.87, S_x = 0.08). A statistical treatment* of the data was then made: thus, the pyridine concentration did not significantly change during 20 hours. In addition, the results also showed that chloroform decomposition** that may have occurred during this standing time did

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* The t-test of significance (63) for the difference between means was used.

** Evidence exists that decomposition occurs in a propyl pyridine-chloroform solution (58).

not measurably affect the pyridine concentration of the aqueous phase.

(b) Effect of the pH of the Aqueous Phase on the Distribution Ratio

Hydrolysis of the nickel in the aqueous phase, to produce water-soluble hydroxo complexes or a precipitate, was then studied. It was considered as a possible explanation of the shift in the distribution curves as the nickel content was varied.

Britton (52) reported that in a solution 0.025M in nickel, precipitation of the hydroxide began at pH 6.66. This value was exceeded for many of the extraction solutions reported in Tables XXIX to XXXI. If hydrolysis had occurred to a significant degree, then the higher the initial concentration of nickel in the system, the greater would the negative error in D have been. This was the effect noticed experimentally.

Therefore the pH was measured at which nickel was precipitated in the presence of pyridine and thiocyanate. The results, in the form of conventional potentiometric titration curves, are shown in Fig. 12. At the neutralization point in curve B, the solution was 5×10^{-4} M in pyridine, 0.3M in potassium thiocyanate, and 5×10^{-3} M in nickel ion, and the pH was 7.3. This solution was similar to that found in the aqueous phase of extraction 4 in Table XXXIX, where the observed curve displacements were very noticeable. However, curve B in Fig. 12 showed that precipitation would be unlikely below pH 8*. These facts indicated that

* Comparison of curves B and C in Fig. 12 indicated that the presence of thiocyanate increased the pH at which precipitation began. This result was expected since pyridine, thiocyanate ion and hydroxyl ion will compete with one another to form a nickel complex. It may readily be calculated that 1.6 equivalents of sodium hydroxide (curve B) would be required to precipitate one equivalent of nickel. This value agrees with the literature (52). In addition, the solubility product constant for nickel hydroxide ($Ni(OH)_2$) was calculated to be 5×10^{-15}. This value also agrees with the literature (55).

FIGURE 12

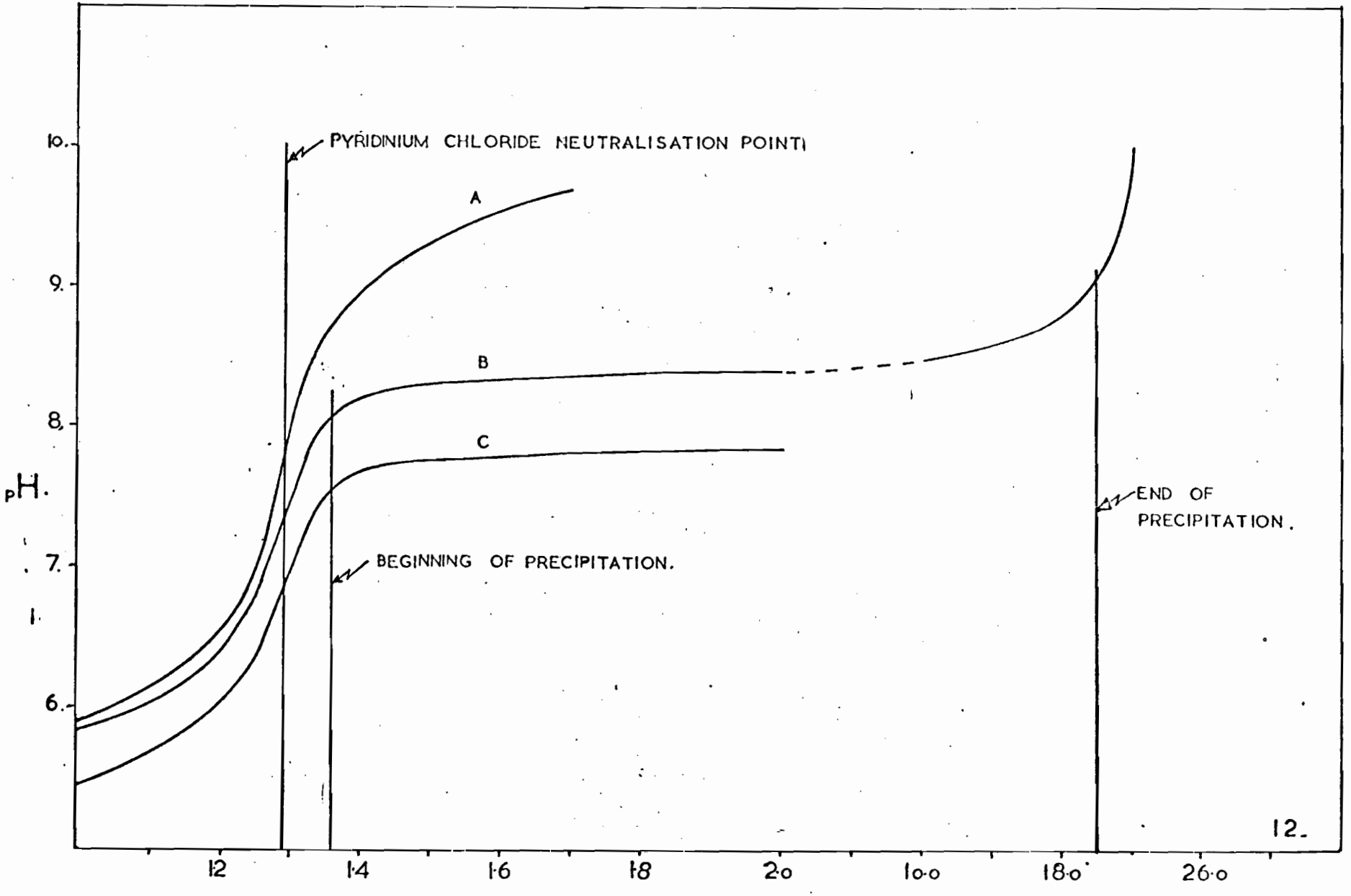
Potentiometric titration curves of 5×10^{-4}-M pyridinium chloride (100 ml) with 0.04-M, carbonate-free sodium hydroxide.

(A) = 0.3-M potassium thiocyanate present.

(B) = 0.3-M potassium thiocyanate and 5×10^{-3}-M nickel chloride present.

(C) = 5×10^{-3}-M nickel chloride present.

See Appendix X for procedure used.


PYRIDINIUM CHLORIDE NEUTRALISATION POINT)
A
B
C
END OF PRECIPITATION.
BEGINNING OF PRECIPITATION.
12.
pH.
10.
9.
8.
7.
6.
1·2
1·4
1·6
1·8
2·0
10·0
18·0
26·0
0·04 -M. SODIUM HYDROXIDE, ML.

precipitation of nickel had not occurred in the extractions.

Confirmation of the above conclusion was sought by carrying out additional extractions, at pH values so low that neither precipitation nor hydrolysis would be expected. The reduction in pH was achieved by the addition of pyridinium chloride to the aqueous phase of the extraction system.

The results are in Table XXXII. They are compared graphically in Figs. 13A and 13B with the results previously obtained in the absence of pyridinium chloride (Table XXIX). The difference in the position of these two sigmoid curves is slight, but statistically significant*. The reason for the difference was sought.

First, it was considered advisable on statistical grounds to repeat some of the experiments in Tables XXIX and XXXII, this time simultaneously. Further, the initial concentrations of pyridine were chosen such that the percent nickel extracted was about the same for the three initial concentrations of nickel chosen. Finally, the concentration of pyridinium chloride was 10^{-3} M, instead of 10^{-2} M**.

The results are in Table XXXIII, and are shown graphically in

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* Since paired observations (identical extractions carried out both in the presence and absence of added pyridinium chloride) were available, then those extractions carried out in the absence of pyridinium chloride could be statistically compared to those extractions carried out in the presence of pyridinium chloride. A standard error of the difference for the paired observations was first calculated. Then a t-test of significance was used. The method has been described in detail by Edwards (64).

** This lower concentration of pyridinium chloride permitted the potentiometric end point of the pyridine titration to be determined more easily.

TABLE XXXII A

Effect of the pyridine concentration, in the presence of pyridinium chloride, on the distribution of nickel between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time: 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Nickel				Pyridine		Pyridinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	27.38	27.36	0	27.36	0	0	0.01	2.93
2	"	26.55	0.787	27.34	40.8	3.12	"	3.67
3	"	23.36	4.20	27.56	81.5	4.68	"	3.85
4	"	18.61	8.59	27.20	122.2	5.44	"	3.94
5	"	13.93	13.70	27.63	163.0	6.66	"	4.02
6	"	9.37	18.10	27.47	203.8	8.28	"	4.10
7	"	5.10	21.83	26.93	244.5	9.08	"	4.16
8	"	2.87	24.46	27.33	285.2	10.1	"	4.17
9	"	1.35	25.96	27.31	326.0	12.1	"	4.32

* 1392 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE XXXII B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for nickel pyridine thiocyanate extractions*

Ext. No.	Nickel				Pyridine		Thiocyanate***	
	Found, M x 10^3				Found, M x 10^3		Found, M x 10^3	
	H_2O	$CHCl_3$	D	E	H_2O	$CHCl_3$**	H_2O	$CHCl_3$
1	5.11	0	0	0	0	0	262.7	0
2	4.96	0.152	0.0307	2.88	0.432	5.57	262.3	0.30
3	4.36	0.814	0.187	15.3	0.649	11.1	261.2	1.63
4	3.48	1.66	0.477	31.5	0.755	16.8	259.5	3.32
5	2.60	2.65	1.02	49.6	0.924	22.4	258.0	5.30
6	1.75	3.50	2.00	66.2	1.15	28.0	256.5	7.00
7	0.955	4.22	4.42	81.1	1.26	33.8	255.3	8.44
8	0.538	4.72	8.78	89.5	1.40	39.5	254.4	9.44
9	0.252	5.02	19.9	95.1	1.68	45.0	254.0	10.0

* Basic data are in Table XXXII A.

** Calculated by difference.

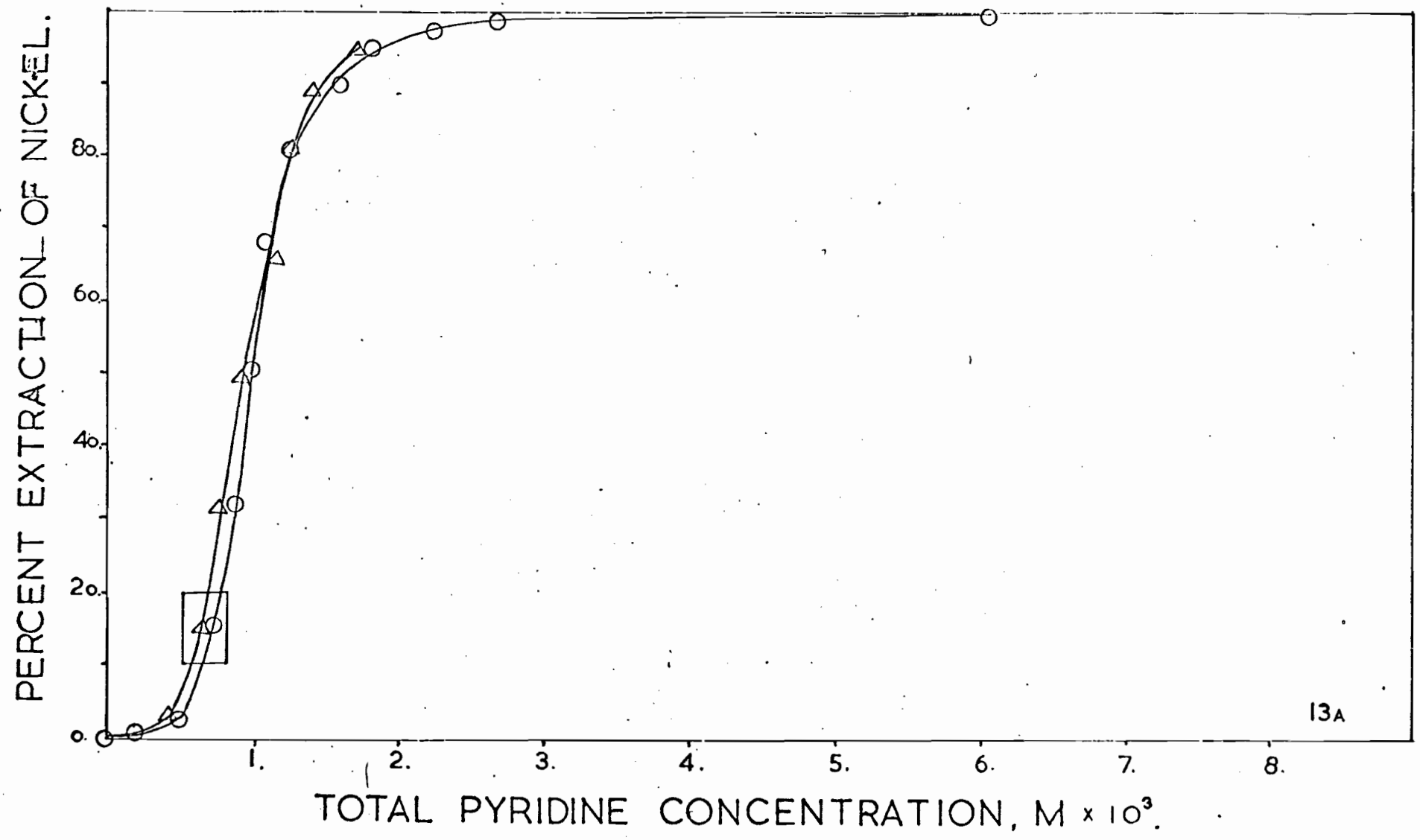
*** The molar ratio of thiocyanate to nickel in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known nickel concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

FIGURES 13A AND 13B

Extraction of nickel pyridine thiocyanate into chloroform, as a function of the total equilibrium concentration of pyridine in the aqueous phase; effect of 0.01-M pyridinium chloride on the percent extraction (13A) and on the distribution ratio (13B).

⊙ = pyridinium chloride absent.

△ = pyridinium chloride present.


PERCENT EXTRACTION OF NICKEL.
0.
20.
40.
60.
80.
1.
2.
3.
4.
5.
6.
7.
8.
TOTAL PYRIDINE CONCENTRATION, M x 10³.
13A

13B.

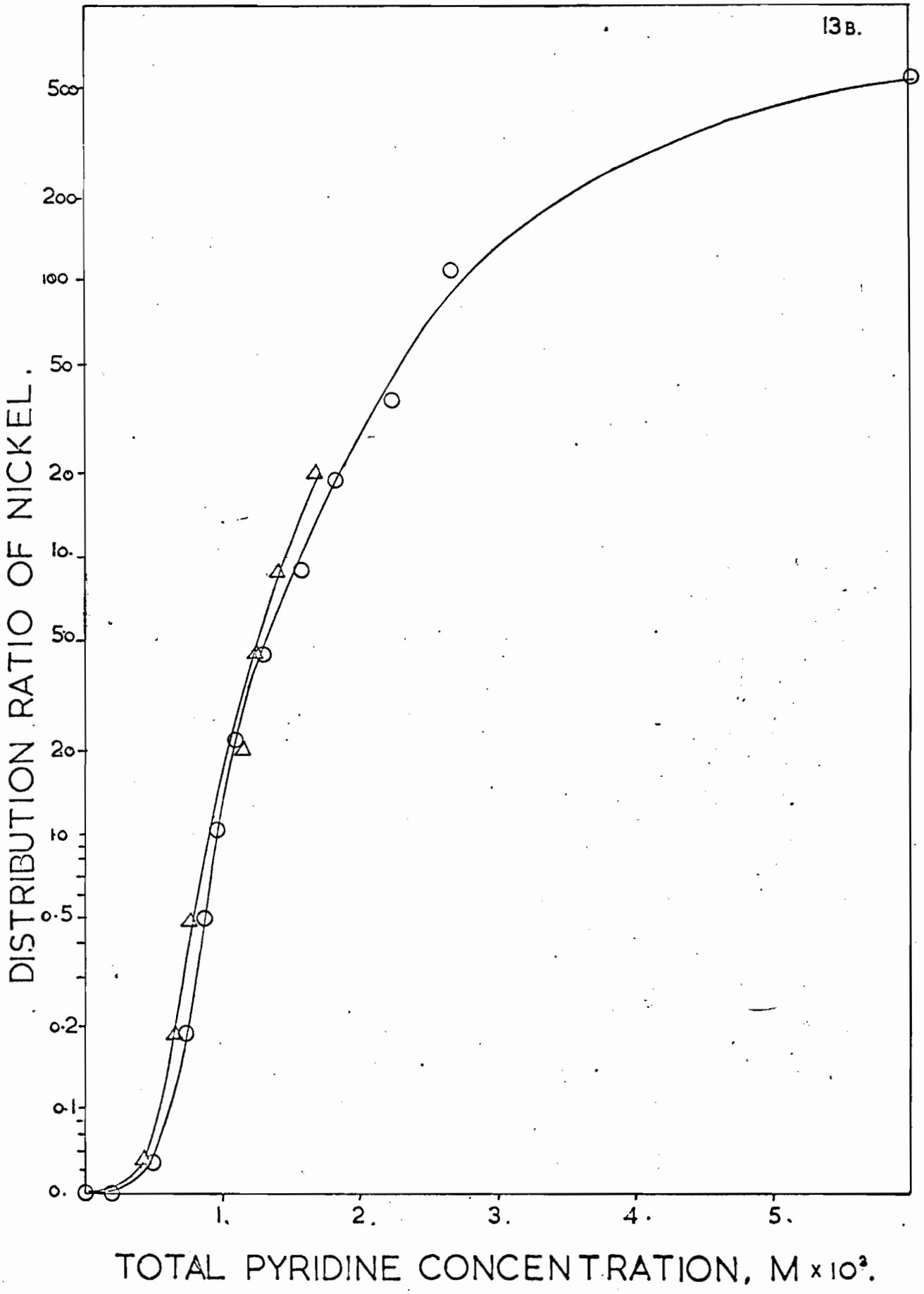

DISTRIBUTION RATIO OF NICKEL.
500
200
100
50
20
10
5
2
1
0.5
0.2
0.1
0.
1.
2.
3.
4.
5.
TOTAL PYRIDINE CONCENTRATION, M x 10³.

TABLE XXXIII A

Effect of the pyridine concentration, in the presence and absence of pyridinium chloride, on the distribution of different amounts of nickel between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Nickel				Pyridine		Pyridinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	27.40	-	4.08	-	78.4	5.47	0	6.86
2	"	-	4.06	-	"	5.53	0	6.90
3	"	-	4.12	-	"	5.22	0.001	5.10
4	"	-	4.18	-	"	5.10	0.001	5.08
5	13.70	-	2.08	-	66.7	4.73	0	6.88
6	"	-	2.08	-	"	4.79	0	6.90
7	"	-	2.16	-	"	4.42	0.001	5.15
8	"	-	2.16	-	"	4.42	0.001	5.11
9	2.740	-	0.463	-	58.8	4.30	0	6.97
10	"	-	0.452	-	"	4.30	0	6.90
11	"	-	0.474	-	"	3.87	0.001	5.12
12	"	-	0.471	-	"	3.98	0.001	5.12

* 1390 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE XXXIII B

Distribution ratio (D), percent extraction (E), and molar concentrations (M) for nickel pyridine thiocyanate extractions*

Ext. No.	Nickel				Pyridine			
	Found, M x 10^3		D	E	Found, M x 10^3		Decrease due to pyridinium chloride	
	H_2O**	$CHCl_3$			H_2O	Average	M x 10^3	Percent
1	4.36	0.791	0.181	14.9	0.758	0.763	0.048	6.3
2	4.36	0.788	0.181	14.9	0.767			
3	4.35	0.799	0.184	15.1	0.724	0.715		
4	4.34	0.811	0.187	15.3	0.707			
5	2.17	0.403	0.186	15.2	0.656	0.660	0.047	7.1
6	2.17	0.403	0.186	15.2	0.664			
7	2.16	0.419	0.194	15.8	0.613	0.613		
8	2.16	0.419	0.194	15.8	0.613			
9	0.425	0.0897	0.211	16.9	0.596	0.596	0.052	8.7
10	0.427	0.0876	0.205	16.5	0.596			
11	0.423	0.0919	0.217	17.3	0.537	0.544		
12	0.424	0.0913	0.215	17.2	0.552			

* Basic data are in Table XXXIII A.

** Calculated by difference.

Fig. 14. These graphs show that two separate phenomena* were occurring. First, for each of the three initial concentrations of nickel, the presence of pyridinium did not appreciably affect the percentage extraction of nickel, but did result in a lower recovery of pyridine from the aqueous phase; second, in either the presence or absence of pyridinium chloride, the extraction curve was progressively displaced to the left as the initial concentration of nickel was decreased.

(c) Effect of the Nature of the Solvent

In order to determine whether or not the effects noted in the preceding paragraph were for some reason connected with the solvent, the experimental study was repeated with benzene as the solvent**. In an orientation study, the effect of pyridine on the distribution of nickel pyridine thiocyanate was studied both in the presence and absence of added pyridinium chloride. The extraction system was found to reach equilibrium during 10 seconds of mechanical shaking. Further, the extraction of nickel in the absence of pyridine was negligible. The

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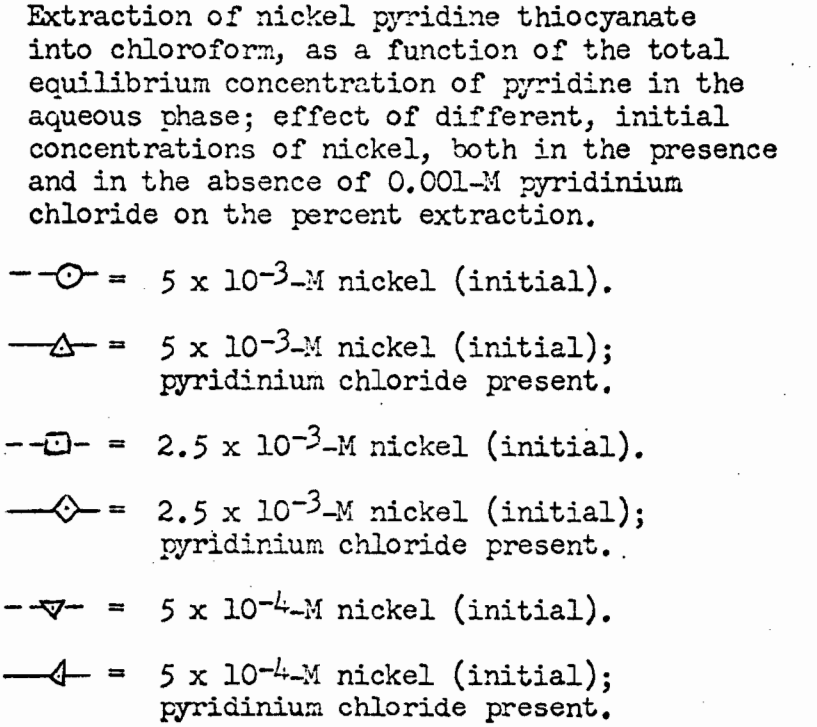
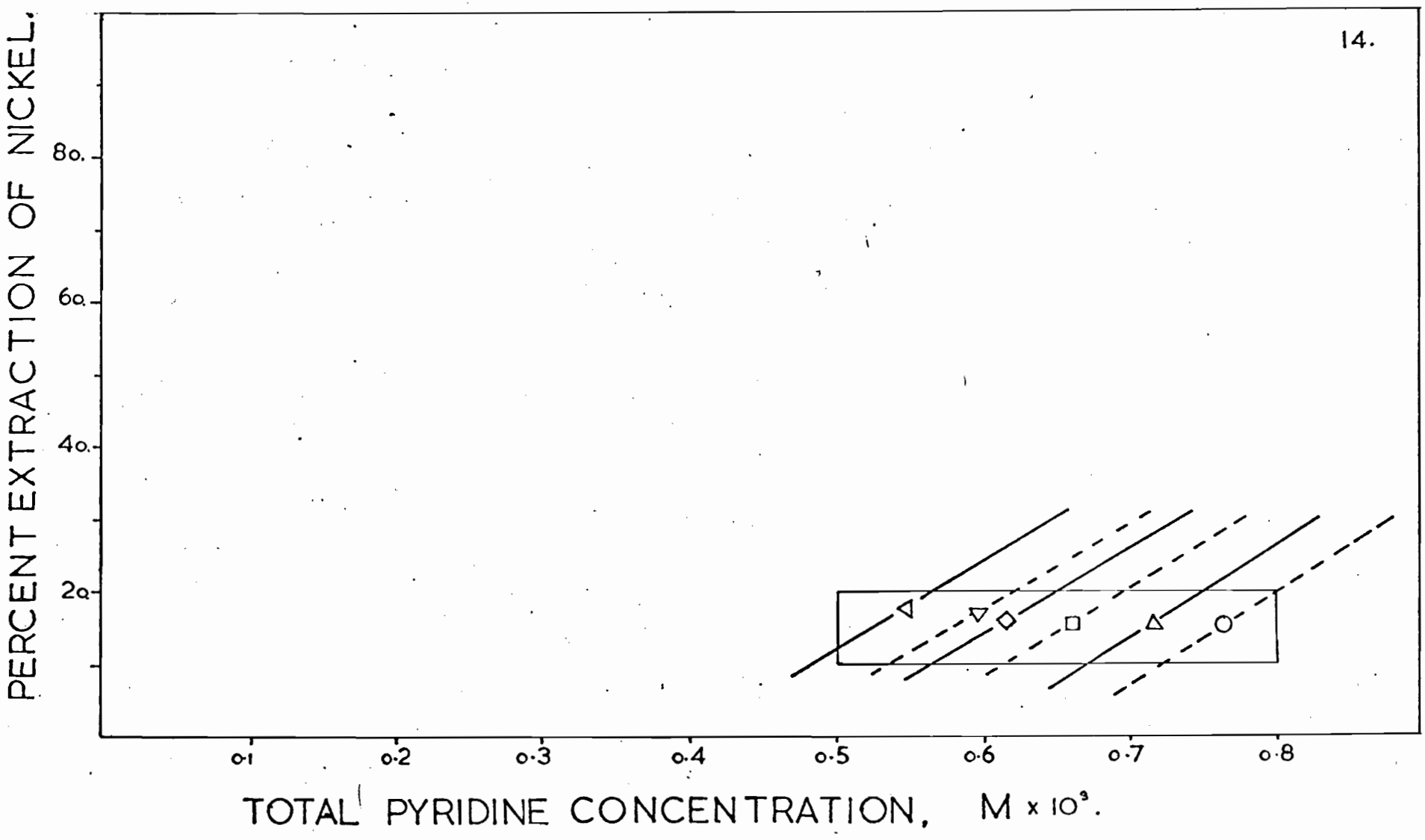
* This observation has a statistical basis: the convention described by Mode (65) states that a result differs from another result if the difference between them exceeds two standard deviations. In Table XXXIII, the pyridine concentrations in the aqueous phase, in the presence and absence of pyridinium chloride, differ by more than this amount (using the standard duration of the pyridine determination given in Table XV; that is 0.01×10^{-3} M). A similar conclusion is drawn upon comparison of the systems containing different amounts of the metal.

** Carbon tetrachloride was an unsatisfactory solvent due both to emulsification and to the low solubility of the nickel pyridine thiocyanate complex (even an initial concentration of nickel of 5×10^{-4} M resulted in the presence of an unwanted solid phase). Benzene was satisfactory provided the initial concentration of nickel did not exceed 2.5×10^{-3} M.

FIGURE 14


Extraction of nickel pyridine thiocyanate into chloroform, as a function of the total equilibrium concentration of pyridine in the aqueous phase; effect of different, initial concentrations of nickel, both in the presence and in the absence of 0.001-M pyridinium chloride on the percent extraction.
= 5 x 10-3-M nickel (initial).
= 5 x 10-3-M nickel (initial); pyridinium chloride present.
= 2.5 x 10-3-M nickel (initial).
= 2.5 x 10-3-M nickel (initial); pyridinium chloride present.
= 5 x 10-4-M nickel (initial).
= 5 x 10-4-M nickel (initial); pyridinium chloride present.
NOTES: (1) Each point is the average of duplicate extractions.
(2) Each line indicates the approximate slope of the extraction curve at the point.


PERCENT EXTRACTION OF NICKEL.
80.
60.
40.
20.
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
TOTAL PYRIDINE CONCENTRATION, M x 10³.

results are in Table XXXIV.

Further extractions were carried out in which the initial concentrations of pyridine were chosen such that the percent nickel extracted was about the same. The initial concentration of nickel was varied both in the presence and absence of pyridinium chloride. The results are given in Table XXXV, and are shown graphically in Fig. 15, along with results from Table XXXIV.

Comparison of Fig. 14 with Fig. 15 showed that the same kind of curve displacements had occurred for both benzene and chloroform. Therefore, the curve displacements were not related to the nature of the solvent.

The two questions that remained unanswered were: (1) why did a decrease in the nickel content of the system produce a shift to the left of the sigmoid distribution curve of nickel? (2) Why did the presence of pyridinium chloride produce lower recoveries of pyridine in the aqueous phase, without changing the distribution ratio of nickel?

The first effect was subsequently sought for and found* in one other system, namely cobalt pyridine thiocyanate. The second effect was sought for and found** in five other systems, namely cobalt pyridine thiocyanate, zinc pyridine thiocyanate, cadmium pyridine thiocyanate, and cobalt 3-picoline (and 4-picoline) thiocyanates (using picolinium chloride). Other systems were not examined for these effects.

Possible reasons for the first effect are suggested in Part VI, but these reasons are without further experimental confirmation.

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* See Part V-4-2.

** See Part V-4-2,3, 4 and 5 for the results.

TABLE XXXIV A

Effect of the pyridine concentration, in the presence and absence of pyridinium chloride, on the distribution of different amounts of nickel between benzene and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : Assumed to be 90 ml.
Mechanical shaking time : As indicated.
Extraction temperature : 25.0°C.

Ext. No.	Mechanical shaking time (sec)	Nickel				Pyridine		Pyridinium chloride molarity	Equil. pH of H_2O phase
		Taken, mg (in H_2O)	Found, mg			Taken, mg (in H_2O)	Found, mg		
			H_2O	C_6H_6	Total		H_2O		
1	600	13.70	-	0.010	-	0	-	0	6.47
2	600	"	-	0.817	-	39.6	10.4	"	6.86
3A	10	"	-	4.10	-	79.2	16.4	"	6.92
3B	600	"	-	4.07	-	"	16.0	"	6.90
3C	1800	"	-	4.10	-	"	16.2	"	6.95
4	600	"	-	8.24	-	118.9	20.3	"	6.95
5	"	"	-	0.835	-	39.6	10.0	0.001	5.39
6	"	"	-	4.08	-	79.2	15.4	"	5.52
7	"	"	-	8.24	-	118.9	19.8	"	5.58
8	"	2.740	-	0.261	-	39.6	10.4	0	6.91
9	"	"	-	1.46	-	79.2	18.4	"	7.00
10	"	"	-	2.32	-	118.9	26.4	"	7.13

* 1400 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE XXXIV B

Distribution ratio (D), percent extraction (E), and molar concentrations (M) for nickel pyridine thiocyanate extractions into benzene*

Ext. No.	Nickel				Pyridine	
	Found, M x 10^3		D	E	Found, M x 10^3	
	H_2O**	C_6H_6			H_2O	C_6H_6**
1	2.59	0.001	0.00039	0.039	-	-
2	2.43	0.155	0.0636	5.98	1.46	4.10
3A	1.82	0.776	0.426	29.9	2.30	8.83
3B	1.82	0.771	0.424	29.8	2.25	8.88
3C	1.82	0.776	0.426	29.9	2.27	8.86
4	1.03	1.56	1.51	60.2	2.85	13.8
5	2.43	0.158	0.0651	6.11	1.41	4.16
6	1.82	0.773	0.424	29.8	2.16	8.96
7	1.03	1.56	1.51	60.2	2.78	13.9
8	0.469	0.0494	0.105	9.53	1.46	4.10
9	0.242	0.277	1.14	53.4	2.59	8.54
10	0.0786	0.440	5.60	84.9	3.71	13.0

* Basic data are in Table XXXIV A.

** Calculated by difference.

TABLE XXXV A

Effect of the pyridine concentration, in the presence and absence of pyridinium chloride, on the distribution of different amounts of nickel between benzene and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : Assumed to be 90 ml.
Mechanical shaking time : 30 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Nickel				Pyridine		Pyridinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	C_6H_6	Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	13.70	-	4.09	-	78.4	16.4	0	6.93
2	"	-	4.04	-	"	16.0	0	6.85
3	"	-	4.14	-	"	15.4	0.001	5.58
4	"	-	4.12	-	"	15.6	0.001	5.50
5	2.740	-	0.760	-	58.8	14.2	0	6.85
6	"	-	0.779	-	"	14.2	0	6.88
7	"	-	0.797	-	"	13.6	0.001	5.58
8	"	-	0.797	-	"	13.6	0.001	5.58

* 1400 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE XXXV B

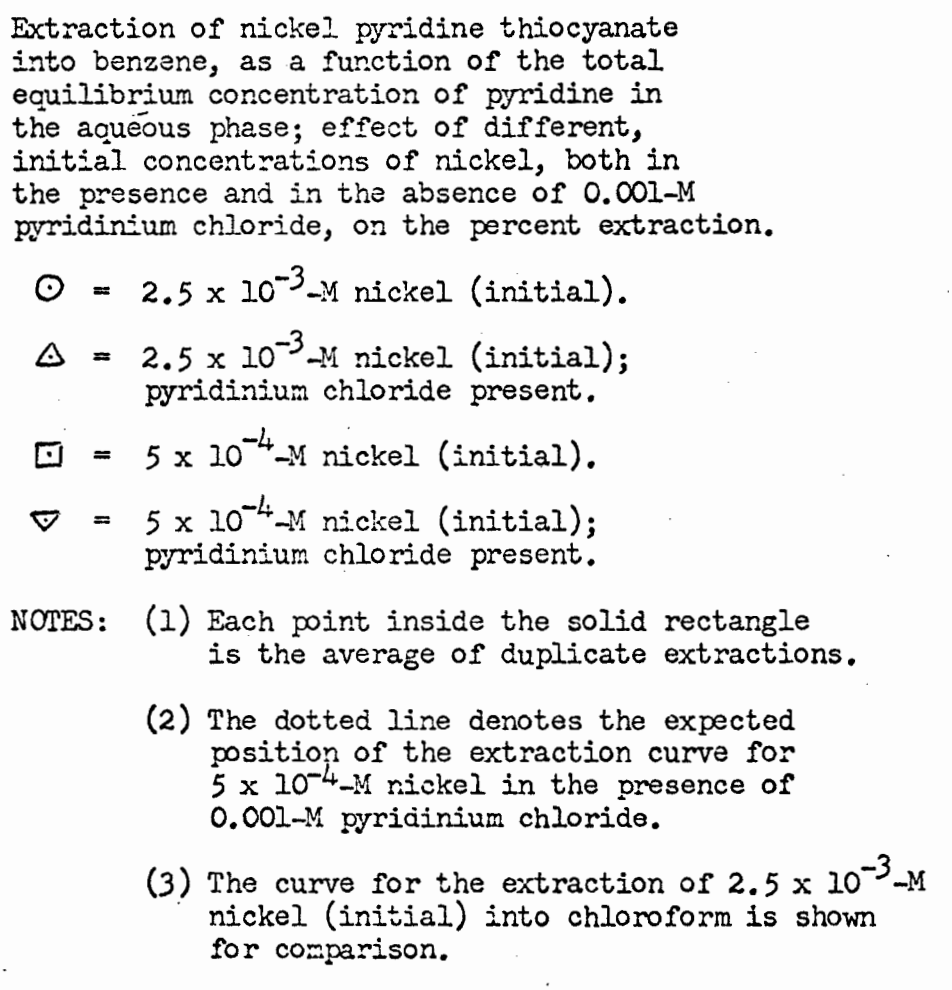
Distribution ratio (D), percent extraction (E), and molar concentrations (M) for nickel pyridine thiocyanate extractions into benzene*

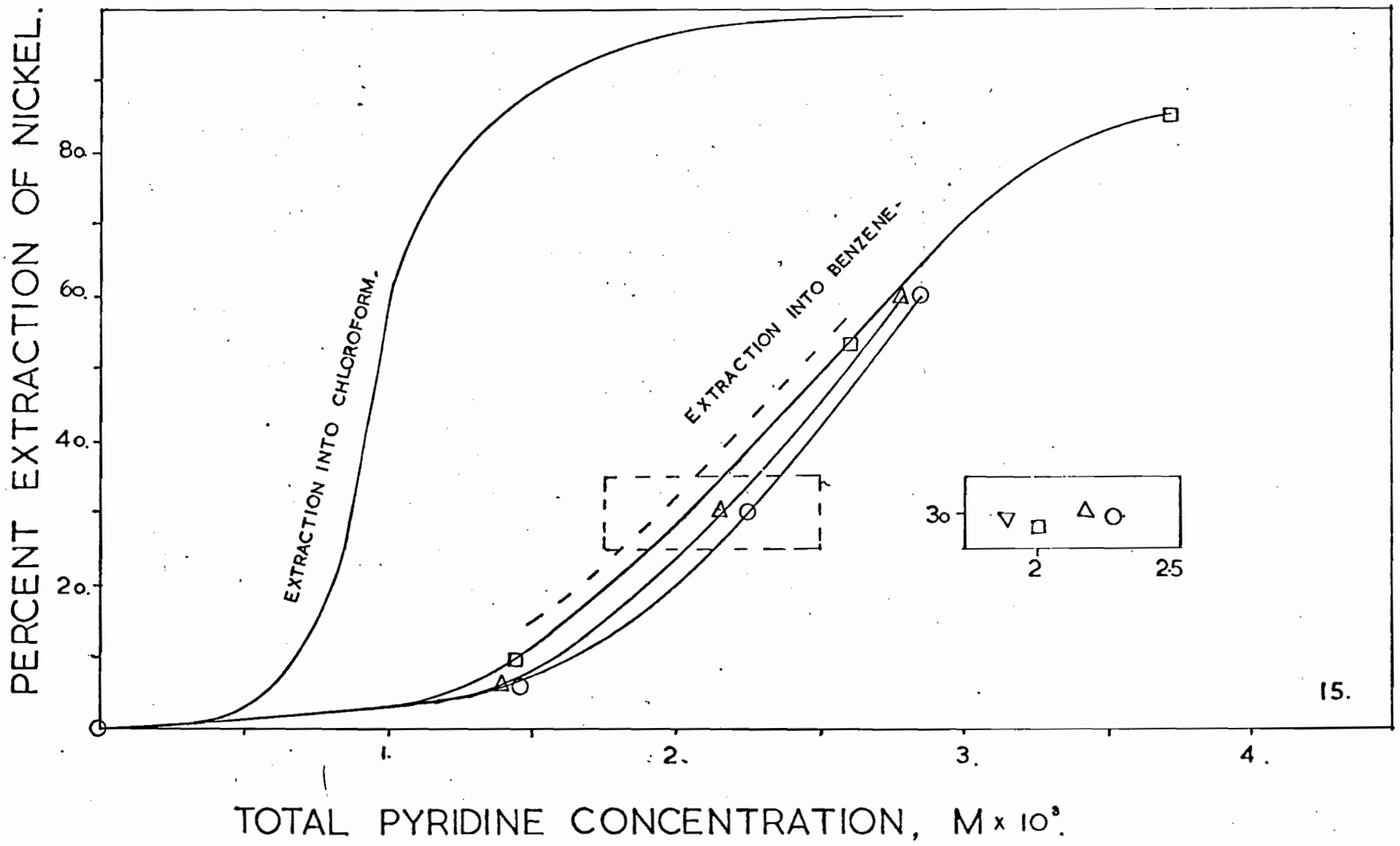
Ext. No.	Nickel				Pyridine			
	Found, M x 10^3		D	E	Found, M x 10^3		Decrease due to pyridinium chloride	
	H_2O**	$CHCl_3$			H_2O	Average	M x 10^3	Percent
1	1.82	0.774	0.425	29.7	2.30	2.28	0.10	4.4
2	1.83	0.765	0.418	29.5	2.25			
3	1.81	0.784	0.433	30.2	2.16	2.18		
4	1.81	0.780	0.431	30.1	2.19			
5	0.375	0.144	0.384	27.7	2.00	2.00	0.09	4.5
6	0.371	0.147	0.396	28.4	2.00			
7	0.368	0.151	0.410	29.1	1.91	1.91		
8	0.368	0.151	0.410	29.1	1.91			

* Basic data are in Table XXXV A.

** Calculated by difference.

FIGURE 15


Extraction of nickel pyridine thiocyanate into benzene, as a function of the total equilibrium concentration of pyridine in the aqueous phase; effect of different, initial concentrations of nickel, both in the presence and in the absence of 0.001-M pyridinium chloride, on the percent extraction.
⊙ = 2.5 x 10⁻³-M nickel (initial).
△ = 2.5 x 10⁻³-M nickel (initial); pyridinium chloride present.
⊡ = 5 x 10⁻⁴-M nickel (initial).
▽ = 5 x 10⁻⁴-M nickel (initial); pyridinium chloride present.
NOTES: (1) Each point inside the solid rectangle is the average of duplicate extractions.
(2) The dotted line denotes the expected position of the extraction curve for 5 x 10⁻⁴-M nickel in the presence of 0.001-M pyridinium chloride.
(3) The curve for the extraction of 2.5 x 10⁻³-M nickel (initial) into chloroform is shown for comparison.


PERCENT EXTRACTION OF NICKEL.
80.
60.
40.
20.
EXTRACTION INTO CHLOROFORM.
EXTRACTION INTO BENZENE.
30
2
25
15.
1.
2.
3.
4.
TOTAL PYRIDINE CONCENTRATION, M x 10³.

The experimental study of the second effect was extended. The distribution ratios of pyridine and the picolines (without metal present) were measured, both in the presence and in the absence of 0.001-M pyridinium (or picolinium) chloride, between chloroform and aqueous 0.3-M solutions of thiocyanate. The results are in Table XXXVI. The pyridine and picoline distribution ratios were significantly* higher in the presence, than in the absence, of pyridinium (or picolinium) chloride. This was also the effect noticed in the metal pyridine and picoline thiocyanate extraction systems previously described.

However, the distribution ratio for pyridine between chloroform and aqueous 0.3-M thiocyanate was later re-measured over a range of pyridine concentrations to see if the distribution ratio changed with pyridine concentration. The results are in Table XXXVII. The distribution ratio of pyridine reported in Table XXXVI (13.0, $S_x = 0.2$) did not agree with that reported in Table XXXVII (14.0, $S_x = 0.3$). Carbon dioxide was suspected of being the cause of the discrepancy. Its possible effect is discussed below.

The solubilities of carbon dioxide, in terms of mole fractions, in water and chloroform have been reported (59) to be, at 20°C, 7×10^{-4}

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* This observation has a statistical basis: the convention described by Mode (65) states that a result differs from another result if the difference between them exceeds two standard deviations. The standard deviation of the extraction and determination of a picoline in the aqueous phase is about one percent (see Tables XVIII, XIX and XX). It is evident from the results in Table XXXVI that the effect of picolinium chloride on the concentration of picoline in the aqueous phase was many times greater than one percent. The distribution ratios of pyridine in the presence and absence of pyridinium chloride were significantly different, as found from the t-test of significance (63) for the difference between means.

TABLE XXXVI

Effect of pyridinium (or picolinium) chloride on the distribution ratio (α) of pyridine (or picoline) between chloroform and aqueous 0.3-M thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Pyridine or Picoline										Pyridinium (or picolinium) chloride molarity
	Reagent	Taken, mg (in H_2O)	Found, mg			Found, M x 10^3			α	Sx	
			H_2O	Sx	$CHCl_3$*	H_2O	Sx	$CHCl_3$*			
1	Pyridine	76.3	5.63	0.10	70.7	0.781	0.010	10.1	13.0	0.2	0
2	"	"	5.13	0.02	71.2	0.712	0.002	10.2	14.3	0.1	0.001
3	2-Picoline	439.8	10.7	-	429.	1.27	-	52.3	41.2	-	0
4	"	"	10.2	-	430.	1.21	-	52.3	43.2	-	0.001
5	3-Picoline	460.2	8.50	-	452.	1.01	-	55.0	54.7	-	0
6	"	"	8.14	-	452.	0.963	-	55.0	57.1	-	0.001
7	4-Picoline	447.6	9.55	-	438.	1.13	-	53.3	47.2	-	0
8	"	"	8.97	-	439.	1.06	-	53.4	50.2	-	0.001

* Calculated by difference.

NOTES: (1) Extractions 1 and 2 are means of 3 replicates.

(2) Extractions 3 - 8 inclusive are means of duplicates.

TABLE XXXVII

Distribution ratio (α) of pyridine between chloroform and aqueous 0.3-M thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Pyridine					
	Taken, mg (in H_2O)	Found, mg		Found, M x 10^3		α**
		H_2O	$CHCl_3$*	H_2O	$CHCl_3$*	
1	0	0	0	0	0	-
2	40.8	2.76	38.0	0.383	5.47	14.3
3	81.5	5.69	75.8	0.790	10.9	13.8
4	122.2	8.75	113.	1.21	16.3	13.5
5	163.0	11.3	152.	1.57	21.8	13.9
6	203.8	13.8	190.	1.92	27.3	14.2
7	244.5	16.8	228.	2.33	32.8	14.1
8	285.2	19.4	266.	2.70	38.2	14.1
9	326.0	22.4	304.	3.12	43.6	14.0
10	815.	54.0	761.	7.55	109.	14.4

* Calculated by difference.

** Mean is 14.0; $s_x = 0.3$; the equation of the least-squares line (101) is

$$\alpha = 14.03 + 2.3 \times 10^{-4}[P]_{T,A}$$

where $[P]_{T,A}$ is the total concentration of pyridine in the aqueous phase.

(0.039M) and 123 x 10^{-4} (0.154M), respectively, under one atmosphere pressure of carbon dioxide. Therefore, under normal atmospheric conditions, the concentrations of carbon dioxide in water and chloroform would be approximately 1.2 x 10^{-5} M and 4.6 x 10^{-5} M, respectively*.

Suppose, for example, that an equilibrated water-chloroform extraction system containing pyridine has a pyridine concentration in the aqueous phase of 8 x 10^{-4} M. If, in the limiting case, the carbon dioxide in the aqueous phase (1.2 x 10^{-5} M) and that in the chloroform phase (4.6 x 10^{-5} M) were to react quantitatively with the pyridine in the aqueous phase according to

$$C_5H_5N + H_2O + CO_2 = C_5H_5NH^+ HCO_3^- \qquad (21)$$

then 7.3 percent of that aqueous pyridine would be present as pyridinium ion**. If the pyridine were to be titrated potentiometrically with a standard solution of hydrochloric acid (see Appendix VI for a procedure) then the total pyridine concentration (pyridine plus pyridinium ion) would be measured. Now the distribution ratio for pyridine would be given by

$$\alpha = \frac{[P]_o}{[P] + [PH^+ HCO_3^-]} \qquad (22)$$

where the subscript o designates the organic phase and the absence of a subscript designates the aqueous phase. However, in the presence of added

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* Based on one liter of air weighing one gram, on air being 0.03 percent carbon dioxide by volume (60), and on carbon dioxide, at that partial pressure, behaving as an ideal gas (61).

** Provided that the phase volumes are equal.

pyridinium chloride, this distribution ratio for pyridine would evidently be reduced, since the pyridinium chloride would shift the equilibrium in equation (21) to the left. Thus, the additive would reduce the effect of carbon dioxide.

Experiments were then carried out in order to determine the effect of carbon dioxide on the pyridine distribution ratio. This ratio was measured in the presence and in the absence of pyridinium chloride, both in the presence and absence of carbon dioxide*. The results are given in Table XXXVIII.

The extractions with carbon dioxide-free chloroform were carried out in a nitrogen atmosphere. In extraction 5 the chloroform was aerated for 30 minutes before use to ensure that carbon dioxide would be present; it was not known with certainty that the chloroform in extractions 1-4 contained carbon dioxide. However, the chloroform used in extraction 5 was obtained from a different manufacturer than that used in extractions 1-4 inclusive. Therefore, extractions 6 and 7 were carried out.

A statistical analysis** of the data in Table XXXVIII showed that neither carbon dioxide nor pyridinium chloride had any measurable effect on the distribution ratio of pyridine between chloroform and aqueous 0.3-M thiocyanate.

It has thus proved impossible to reconcile the data of Tables

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* In these experiments, carbon dioxide was removed from the chloroform before use (see Appendix I for details). The smaller concentration in water was ignored.

** The t-test of significance (63) for the difference between means was used. An inter-comparison of all the data in Table XXXVIII showed that only extractions 1 and 7 were significantly different. This result could reasonably be attributed to chance.

TABLE XXXVIII

Effect of carbon dioxide, in the presence and absence of pyridinium chloride, on the distribution ratio (α) of pyridine between chloroform and aqueous 0.3-M thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Pyridine									Pyridinium chloride molarity	$CHCl_3$ grade
	Taken, mg (in H_2O)	Found, mg			Found, M x 10^3			α	Sx		
		H_2O**	Sx	$CHCl_3$*	H_2O**	Sx	$CHCl_3$*				
1	79.8	5.44	0.08	74.4	0.755	0.011	1.07	14.2	0.2	0	CO_2-free
2	"	5.43	0.20	74.4	0.754	0.028	1.07	14.2	0.5	0.001	"
3	"	5.41	0.14	74.4	0.751	0.020	1.07	14.3	0.4	0	Reagent
4	"	5.51	0.04	74.3	0.765	0.006	1.07	14.0	0.1	0.001	"
5	77.8	5.30	0.18	72.5	0.736	0.025	1.04	14.1	0.5	0	"
6	"	5.40	0.07	72.4	0.750	0.010	1.04	13.9	0.2	0.001	"
7	"	5.46	0.13	72.3	0.758	0.016	1.04	13.7	0.3	0	"

* Calculated by difference.

** Means of 4 replicates.

NOTES: (1) The mean value of the distribution ratio was 14.1; its mean standard deviation, Sx, was 0.3.

(2) The chloroform used in extractions 5, 6 and 7 was from a different manufacturer than that used in extractions 1, 2, 3 and 4.

(3) The chloroform used in extractions 5 and 6 was aerated for 30 minutes before use to ensure that carbon dioxide was present.

(4) See Appendix I for the preparation of carbon dioxide-free chloroform.

XXXVII and XXXVIII with the contradicting data of Table XXXVI, on the distribution ratio of pyridine. Moreover, the shift that occurred in the sigmoid curves for the extraction of metal pyridine thiocyanates, when pyridinium chloride was added remains unexplained. However, these shifts do seem to be attributable to the effect of pyridinium chloride on the distribution ratio of pyridine, and not on that of the metal.

The extractions of cobalt 3-picoline (and 4-picoline) thiocyanates were made both in the present and in the absence of picolinium chloride (see Part V-4-5). It was found that the presence of picolinium chloride caused a statistically-significant displacement of the extraction curve to the left. In contrast to similar systems containing pyridine, these results could be explained by means of a change in the distribution ratio of the corresponding picoline. The distribution ratios of 3-picoline and of 4-picoline between chloroform and aqueous 0.3-M solutions of potassium thiocyanate were measured, on several different occasions, both in the presence and absence of the corresponding picolinium chloride. The results are in Table XXXIX. A statistical analysis* proved that the presence of picolinium chloride caused a significant increase in the distribution ratio of 3-picoline and of 4-picoline.

The results given in Tables XXXVIII and XXXIX were obtained after much of the experimental work in the present investigation had been carried out. It was decided to determine the remaining extraction curves (nickel, zinc and cadmium picoline thiocyanates) only in the presence of the corresponding picolinium chloride. The reason was that

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* The t-test of significance (63) for the difference between means was used.

TABLE XXXIX

Effect of picolinium chloride on the distribution ratio (α) of 3-picoline (and 4-picoline) between chloroform and aqueous 0.3-M thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	3-Picoline						Picolinium chloride molarity
	Taken, mg (in H_2O)	Found, mg H_2O**	Found, mg $CHCl_3$*	Found, M x 10^3 H_2O**	Found, M x 10^3 $CHCl_3$*	α	
1	409.5	7.39	402	0.875	48.9	55.9	0
2	"	7.64	402	0.904	48.9	54.1	"
3	"	7.43	402	0.880	48.9	55.6	"
4***	460.2	8.50	452	1.01	55.0	54.7	"
5	809.0	15.2	794	1.80	96.3	53.5	"
6	409.5	7.14	402	0.845	48.9	57.9	0.001
7	"	7.28	402	0.862	48.9	56.7	"
8	"	7.35	402	0.870	48.9	56.2	"
9***	460.2	8.14	452	0.963	55.0	57.1	"
10	809.0	14.0	795	1.66	96.4	58.1	"
		4-Picoline					
11	379.6	7.85	372	0.929	45.3	48.8	0
12	"	8.03	372	0.950	45.3	47.7	"
13	"	8.20	371	0.970	45.2	46.6	"
14	"	8.14	371	0.963	45.2	46.9	"
15	"	8.24	371	0.975	45.2	46.4	"
16***	447.6	9.55	438	1.13	53.3	47.2	"
17	759.2	16.2	743	1.92	90.1	47.0	"
18	379.6	7.63	372	0.903	45.3	50.2	0.001
19	"	7.77	372	0.919	45.3	49.3	"
20	"	7.85	372	0.929	45.3	48.8	"
21***	447.6	8.97	439	1.06	53.4	50.2	"
22	759.2	15.4	744	1.83	90.2	49.3	"

* Calculated by difference.

** Means of duplicates.

*** Data from Table XXXVI.

NOTE:

Ext. No.	Mean	Sx
1 - 5	54.7	1.0
6 - 10	57.2	0.8
11 - 17	47.2	0.8
18 - 22	49.6	0.6

in actual analytical separations, the solutions would probably need to be acidic to prevent hydrolysis of some metals. Moreover, the pyridinium-pyridine (or picolinium-picoline) system constituted a potentially useful buffer.

4-2. Cobalt Pyridine Thiocyanate

The distribution of cobalt pyridine thiocyanate between chloroform and aqueous solutions of 0.3-M thiocyanate was studied as a function of the equilibrium concentration of pyridine. Two different, initial concentrations of cobalt were used, 0.0025M and 0.0005M. The results are in Tables XL and XLI. Plots of E and D versus the total equilibrium concentration of pyridine in the aqueous phase are shown in Figs. 16A and 16B, respectively; they show a displacement to the left of the extraction or distribution curve when a smaller concentration of cobalt was used in the extraction system. This effect was also noticed in nickel pyridine thiocyanate extraction systems*.

The cobalt pyridine thiocyanate extraction systems specified above were also studied in the presence of pyridinium chloride. The results are in Tables XLII and XLIII. A plot of E versus the total equilibrium concentration of pyridine in the aqueous phase is shown, for each of the cobalt concentrations, in Figs. 17A and 17B. The corresponding data obtained in the absence of pyridinium chloride are also shown. It was evident, for each cobalt concentration, that the presence of pyridinium chloride resulted in a small but statistically-significant**

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* See Part V-4-1 for details.

** See *, page 125.

TABLE XL A

Effect of the pyridine concentration on the distribution of cobalt between chloroform and aqueous thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cobalt				Pyridine		Thiocyanate		Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O	Taken, mg (in H_2O)	Found, mg $CHCl_3$	
1	13.84	-	0	-	0	0	1429	-	5.20
2	"	13.70	0.0736	13.77	98.1	7.32	"	0.60	6.74
3	"	12.74	1.08	13.82	196.2	13.3	"	2.2	6.79
4R	"	10.14	3.68	13.82	294.3	19.3	"	7.5	6.97
5	"	6.86	6.86	13.72	392.3	25.0	"	14.0	7.03
6	"	4.27	9.62	13.89	490.5	29.9	"	19.5	7.11
7	"	2.46	11.34	13.80	588.6	35.4	"	23.2	7.15
8	"	1.45	12.36	13.81	686.7	41.2	"	25.1	7.19
9	"	0.901	12.93	13.83	784.2	47.5	"	26.1	7.22
10	"	0.196	-	-	1175	73.4	"	-	7.30

NOTE: Extraction 4R is the mean of 4 replicates.

TABLE XL B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for cobalt pyridine thiocyanate extractions*

Ext. No.	Cobalt				Pyridine		Thiocyanate		Molar ratio of thiocyanate to cobalt in $CHCl_3$ phase
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O**	$CHCl_3$	
1	2.58**	0	0	0	0	0	-	-	-
2	2.55	0.0142	0.00557	0.54	1.02	13.1	269.7	0.12	8.5
3	2.38	0.208	0.0873	7.79	1.84	26.3	270.0	0.43	2.07
4R	1.89	0.709	0.375	26.6	2.68	39.6	269.4	1.46	2.03
5	1.28	1.32	1.03	50.0	3.48	52.6	268.3	2.73	2.07
6	0.799	1.85	2.31	69.2	4.17	65.9	267.3	3.80	2.05
7	0.461	2.18	4.73	82.1	4.94	79.0	267.2	4.52	2.07
8	0.272	2.37	8.72	89.5	5.76	92.1	267.2	4.88	2.06
9	0.169	2.48	14.7	93.6	6.64	105.	267.2	5.07	2.04
10	0.0370	2.60**	70.2	98.6	10.3	156.	-	-	-

* Basic data are in Table XL A.

** Calculated by difference.

TABLE XLI A

Effect of the pyridine concentration on the distribution of cobalt between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cobalt				Pyridine		Equil. pH of
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O	H_2O phase
1	2.768	2.774	0.0141	2.788	97.9	6.78	6.65
2	"	2.550	0.225	2.775	195.9	13.3	6.73
3	"	1.942	0.847	2.789	293.8	19.8	7.00
4	"	1.204	1.605	2.809	391.7	25.9	7.02
5	"	0.653	2.113	2.766	489.7	32.6	7.07
6	"	0.368	2.418	2.786	587.6	37.7	7.13
7	"	0.215	2.557	2.772	685.4	44.5	7.17
8	"	0.137	2.628	2.765	776.2	50.0	7.23

* 1429 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE XLI B

Distribution ratio (D), percent extraction (E), and molar concentrations (M) for cobalt pyridine thiocyanate extractions*

Ext. No.	Cobalt				Pyridine		Thiocyanate***	
	Found, M x 10^3		D	E	Found, M x 10^3		Found, M x 10^3	
	H_2O	$CHCl_3$			H_2O	$CHCl_3$**	H_2O	$CHCl_3$
1	0.517	0.00272	0.00527	0.505	0.941	13.1	270.0	0.0054
2	0.475	0.0435	0.0917	8.14	1.84	26.3	270.3	0.0870
3	0.363	0.163	0.449	30.3	2.75	39.3	270.3	0.326
4	0.225	0.309	1.37	57.1	3.60	52.4	270.3	0.618
5	0.122	0.406	3.33	76.4	4.55	65.4	270.4	0.812
6	0.0689	0.464	6.73	86.7	5.26	78.7	270.4	0.928
7	0.0403	0.490	12.2	92.2	6.22	91.6	270.7	0.980
8	0.0257	0.503	19.6	95.0	7.00	104	271.0	1.01

* Basic data are in Table XLI A.

** Calculated by difference.

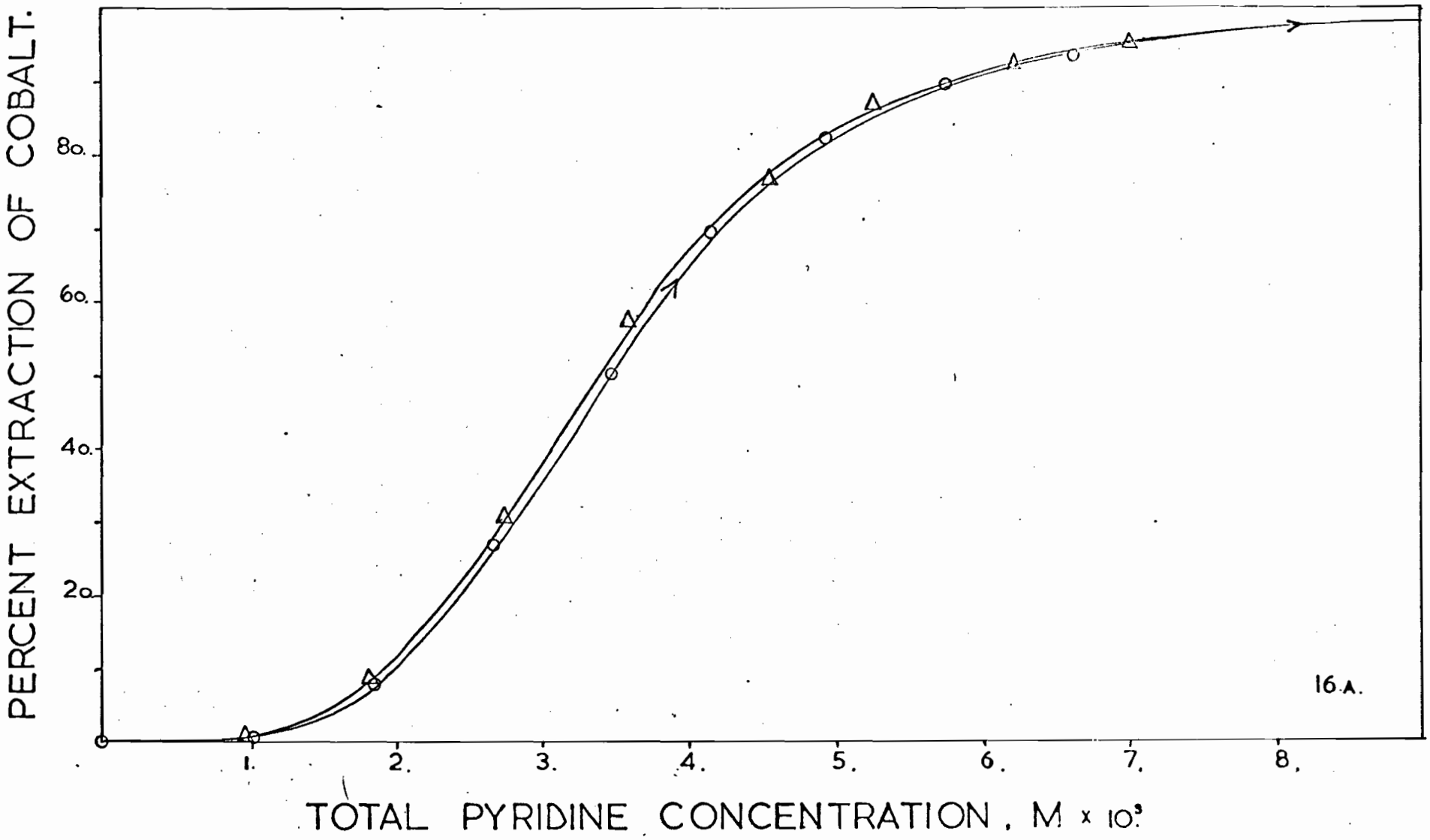
*** The molar ratio of thiocyanate to cobalt in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known cobalt concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

FIGURES 16A AND 16B

Extraction of cobalt pyridine thiocyanate into chloroform, as a function of the total equilibrium concentration of pyridine in the aqueous phase; effect of different, initial concentrations of cobalt on the percent extraction (16A) and on the distribution ratio (16B).

⊙ = 2.5×10^{-3}-M cobalt (initial).

△ = 5×10^{-4}-M cobalt (initial).


PERCENT EXTRACTION OF COBALT.
80.
60.
40.
20.
1.
2.
3.
4.
5.
6.
7.
8.
TOTAL PYRIDINE CONCENTRATION, M x 10³
16.A.

16 B.

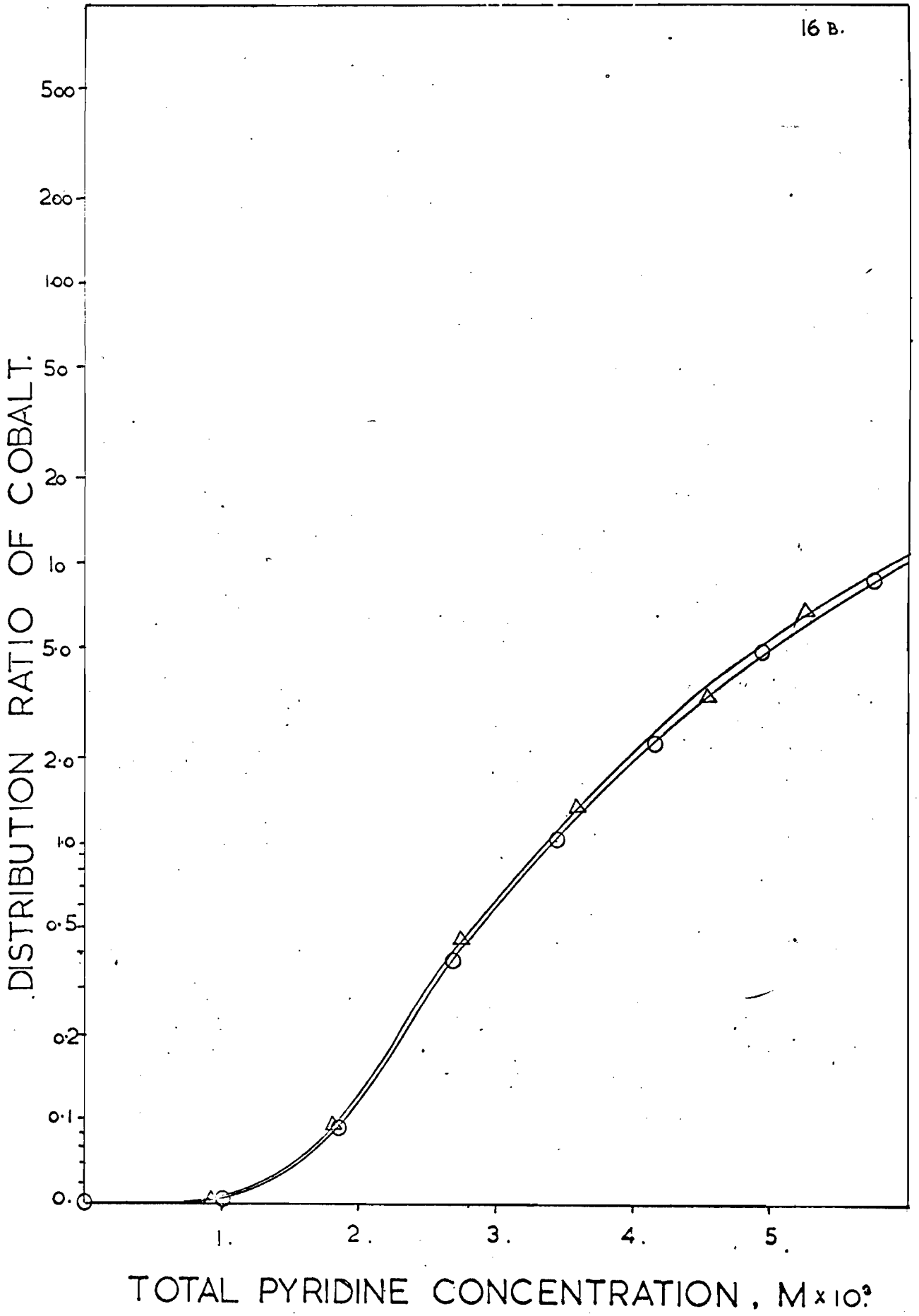

DISTRIBUTION RATIO OF COBALT.
500
200
100
50
20
10
5·0
2·0
1·0
0·5
0·2
0·1
0·
1.
2.
3.
4.
5.
TOTAL PYRIDINE CONCENTRATION, M x 10³

TABLE XLII A

Effect of the pyridine concentration, in the presence of pyridinium chloride, on the distribution of cobalt between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cobalt				Pyridine		Pyridinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	13.84	-	0	-	0	-	0.001	-
2	"	-	0.0751	-	97.9	6.96	"	5.53
3	"	-	1.10	-	195.9	13.4	"	5.57
4	"	-	3.68	-	293.8	18.5	"	5.64
5	"	-	6.92	-	391.8	24.0	"	5.76
6	"	4.33	-	-	489.7	29.0	"	5.88
7	"	2.49	-	-	587.6	34.6	"	5.98
8	"	0.898	-	-	783.5	48.3	"	6.10
9	"	0.189	-	-	1175	72.8	"	6.30

* 1429 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE XLII B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for cobalt pyridine thiocyanate extractions*

Ext. No.	Cobalt				Pyridine		Thiocyanate***	
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O	$CHCl_3$
1	2.58**	0	0	0	-	-	270.0	0
2	2.44**	0.0145	0.00594	0.57	0.966	13.1	269.7	0.029
3	2.37**	0.212	0.0895	7.96	1.86	26.1	269.5	0.42
4	1.90**	0.709	0.373	26.6	2.57	39.5	269.3	1.42
5	1.29**	1.33	1.03	50.0	3.34	52.6	268.3	2.66
6	0.810	1.83**	2.26	68.7	4.04	66.0	267.8	3.66
7	0.466	2.18**	4.68	82.0	4.83	79.1	267.2	4.36
8	0.168	2.48**	14.8	93.7	6.75	105	267.2	4.96
9	0.0357	2.60**	72.8	98.7	10.2	156	268.5	5.20

* Basic data are in Table XLII A.

** Calculated by difference.

*** The molar ratio of thiocyanate to cobalt in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known cobalt concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

TABLE XLIII A

Effect of the pyridine concentration, in the presence of pyridinium chloride, on the distribution of cobalt between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cobalt				Pyridine		Pyridinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	2.768	2.780	0.0148	2.795	97.9	6.33	0.001	5.28
2	"	2.580	0.238	2.818	196.7	13.1	"	5.53
3	"	1.930	0.863	2.793	295.5	19.5	"	5.73
4	"	1.190	1.612	2.802	394.3	25.4	"	5.89
5	"	0.648	2.122	2.770	493.0	31.8	"	5.93
6	"	0.361	2.400	2.761	591.8	37.7	"	6.10

* 1429 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE XLIII B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for cobalt pyridine thiocyanate extractions*

Ext. No.	Cobalt				Pyridine		Thiocyanate***	
	Found, M x 10^3		D	E	Found, M x 10^3		Found, M x 10^3	
	H_2O	$CHCl_3$			H_2O	$CHCl_3$**	H_2O	$CHCl_3$
1	0.518	0.00286	0.00552	0.53	0.879	12.9	270.0	0.0057
2	0.499	0.0459	0.0920	8.17	1.82	26.1	270.0	0.0918
3	0.361	0.166	0.460	30.8	2.71	39.2	270.3	0.332
4	0.222	0.310	1.40	57.6	3.54	52.4	270.3	0.620
5	0.121	0.408	3.37	76.6	4.43	65.4	270.5	0.816
6	0.0676	0.461	6.82	87.0	5.26	78.5	270.5	0.922

* Basic data are in Table XLIII A.

** Calculated by difference.

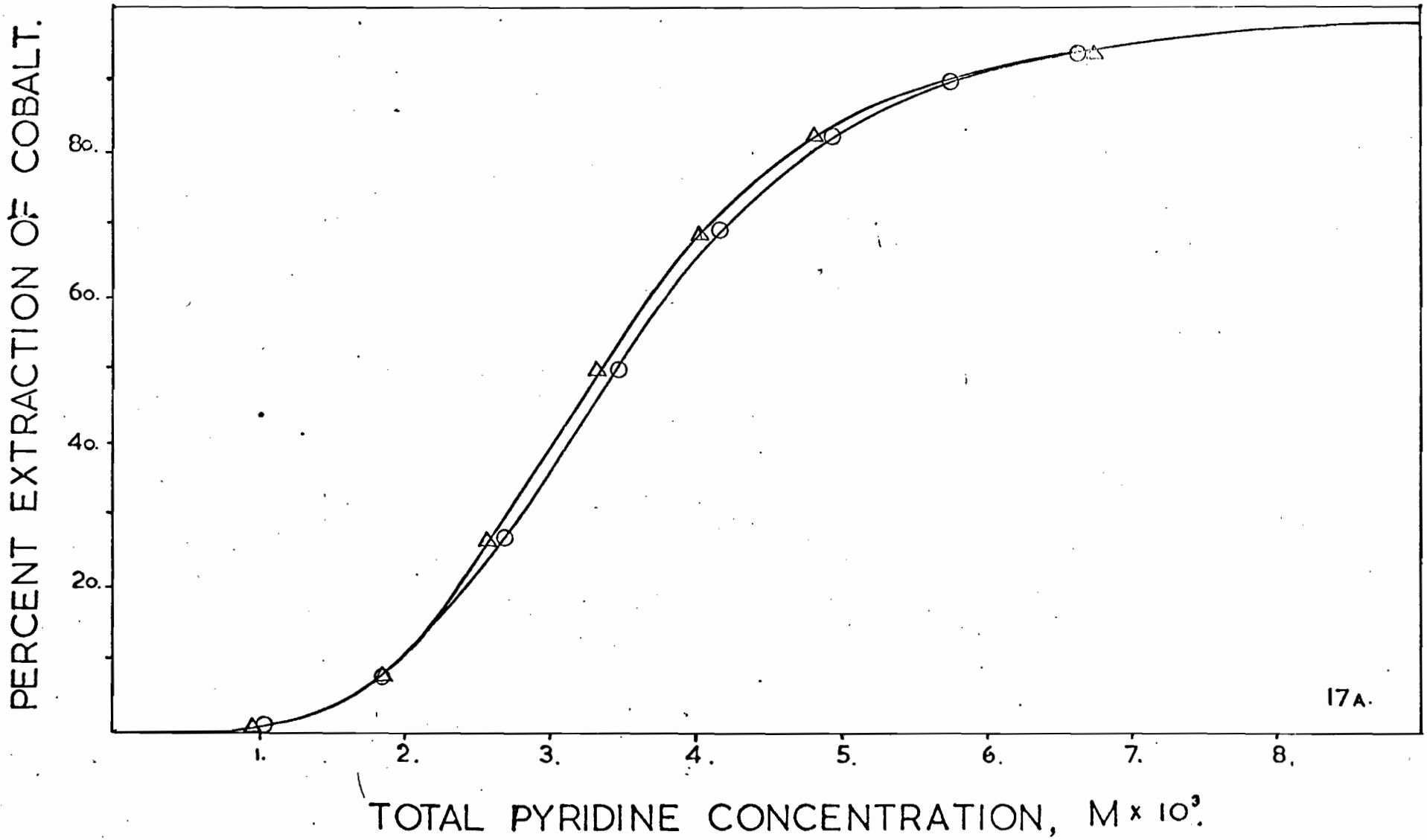
*** The molar ratio of thiocyanate to cobalt in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known cobalt concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

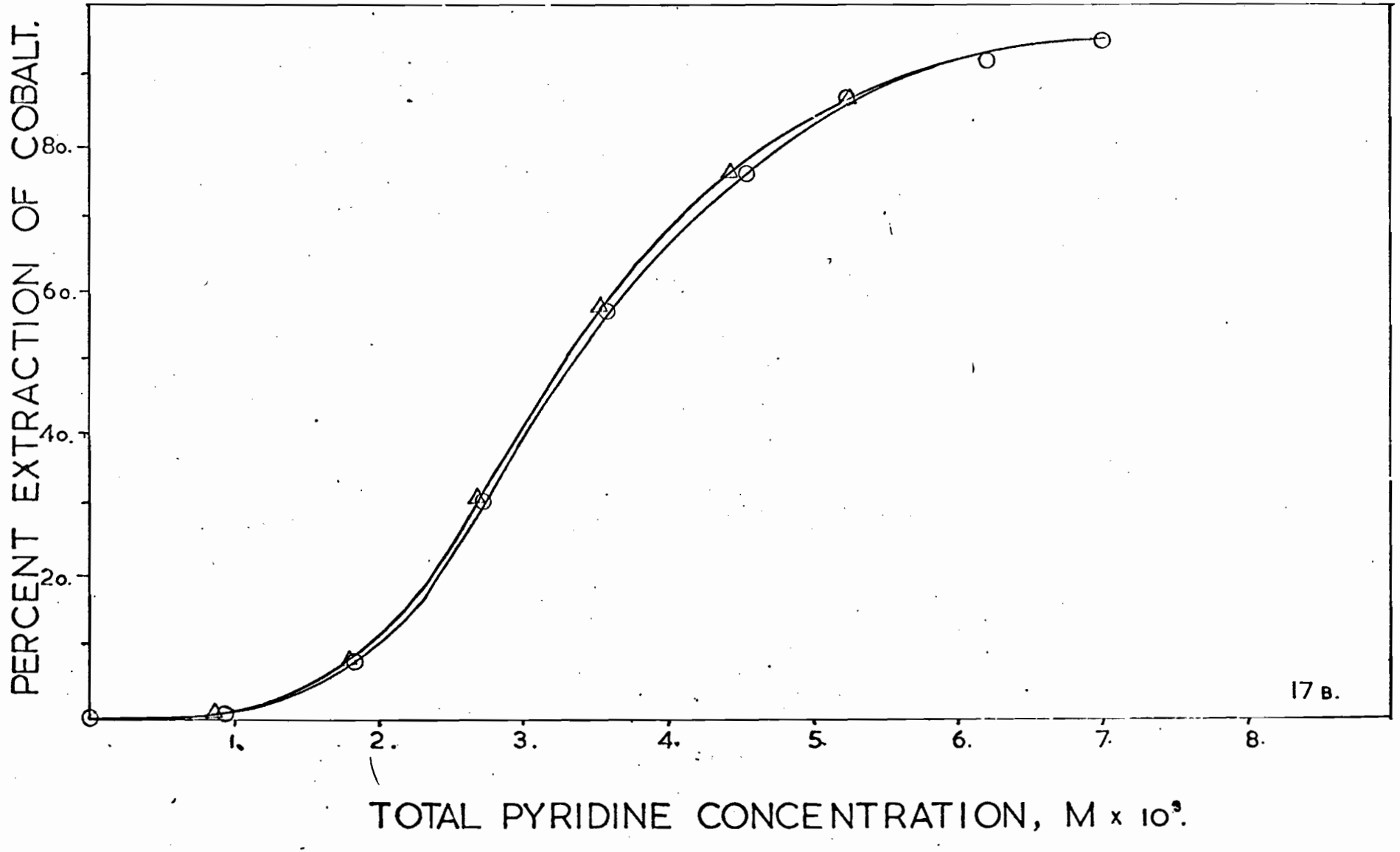
FIGURES 17A AND 17B

Extraction of cobalt pyridine thiocyanate into chloroform, as a function of the total equilibrium concentration of pyridine in the aqueous phase; effect of 0.001-M pyridinium chloride on the percent extraction of 2.5×10^{-4}-M cobalt (17A) and on the percent extraction of 5×10^{-4}-M cobalt (17B).

⊙ = pyridinium chloride absent.

△ = pyridinium chloride present.


PERCENT EXTRACTION OF COBALT.
80.
60.
40.
20.
1.
2.
3.
4.
5.
6.
7.
8.
TOTAL PYRIDINE CONCENTRATION, M x 10³.
17A.


PERCENT EXTRACTION OF COBALT.
80.
60.
40.
20.
1.
2.
3.
4.
5.
6.
7.
8.
TOTAL PYRIDINE CONCENTRATION, M x 10³.
17 B.

displacement of the extraction curve to the left. This same effect was also noticed in nickel pyridine thiocyanate extraction systems*.

4-3. Zinc Pyridine Thiocyanate

The distribution of zinc pyridine thiocyanate between chloroform and aqueous solutions of 0.3-M thiocyanate was studied, both in the presence and absence of pyridinium chloride, as a function of the equilibrium concentration of pyridine. The results are in Tables XLIV and XLV. The plots of E and D against the total equilibrium concentration of pyridine in the aqueous phase are shown in Figs. 18A and 18B, respectively. It was evident that the presence of pyridinium chloride resulted in a small, but statistically-significant** displacement of the extraction curve to the left. This was the same effect noticed in both nickel and cobalt pyridine thiocyanate extraction systems***.

Although not determined experimentally, it was expected that a reduction of the initial concentration of zinc in the extraction system would result, as for nickel and cobalt pyridine thiocyanate systems, in a small displacement of the extraction curve to the left.

4-4. Cadmium Pyridine Thiocyanate

The distribution of cadmium pyridine thiocyanate between chloroform and aqueous solutions of 0.3-M thiocyanate was studied, both in the presence and absence of pyridinium chloride, as a function of the equi-

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* See Part V-4-1 for details.

** See *, page 125.

*** See Parts V-4-1 and 2, respectively, for details.

TABLE XLIV A

Effect of the pyridine concentration on the distribution of zinc between chloroform and aqueous thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Zinc				Pyridine		Thiocyanate		Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O	Taken, mg (in H_2O)	Found, mg $CHCl_3$	
1	30.39	-	0	-	0	-	1389	-	-
2	"	28.56	1.996	30.56	39.7	2.34	"	3.67	5.83
3	"	24.60	5.99	30.59	79.4	4.71	"	10.8	6.01
4	"	19.98	10.45	30.43	119.2	6.92	"	18.7	6.04
5	"	15.94	14.45	30.39	158.9	9.00	"	25.9	6.27
6	"	12.23	18.16	30.39	202.4	10.4	"	32.3	6.42
7	"	9.76	20.58	30.34	238.3	13.0	"	37.0	6.37
8	"	7.67	22.65	30.32	278.0	15.3	"	40.5	6.45
9	"	6.06	24.30	30.36	317.8	17.3	"	43.1	6.50
10	"	4.89	25.42	30.31	357.5	19.8	"	45.0	6.58
11	"	3.94	26.45	30.39	404.8	22.9	"	47.4	6.74
12	"	1.75	28.52	30.27	607.2	35.4	"	51.1	6.88
13R	"	1.02	29.33	30.35	809.6	48.5	"	52.3	6.96
14	"	0.638	29.75	30.39	1012.	62.4	"	53.2	7.04

NOTE: Extraction 13R is the mean of 4 replicates.

TABLE XLIV B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for zinc pyridine thiocyanate extractions*

Ext. No.	Zinc				Pyridine		Thiocyanate		Molar ratio of thiocyanate to zinc in $CHCl_3$ phase
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O**	$CHCl_3$	
1	5.11**	0	0	0	-	-	-	-	-
2	4.79	0.348	0.0727	6.55	0.324	5.39	261.4	0.720	2.22
3	4.13	1.043	0.253	19.7	0.653	10.7	260.0	2.13	2.04
4	3.35	1.820	0.544	34.5	0.959	16.2	259.0	3.66	2.01
5	2.68	2.52	0.940	47.6	1.25	21.6	257.5	5.08	2.03
6	2.05	3.16	1.54	59.8	1.45	27.6	256.8	6.32	2.00
7	1.64	3.58	2.18	67.9	1.80	32.4	255.7	7.23	2.02
8	1.29	3.93	3.05	74.8	2.13	37.8	255.4	7.92	2.02
9	1.02	4.21	4.13	80.2	2.41	43.1	255.0	8.42	2.00
10	0.823	4.41	5.36	83.9	2.76	48.4	255.0	8.79	1.99
11	0.663	4.58	6.91	87.1	3.19	54.8	254.5	9.26	2.02
12	0.295	4.93	16.7	94.2	4.94	81.9	254.2	10.1	2.04
13R	0.172	5.06	29.4	96.7	6.79	108.6	254.6	10.2	2.01
14	0.108	5.12	47.4	98.0	8.75	135.2	255.0	10.3	2.02

* Basic data are in Table XLIV A.

** Calculated by difference.

TABLE XLV A

Effect of the pyridine concentration, in the presence of pyridinium chloride, on the distribution of zinc between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Zinc				Pyridine		Pyridinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	30.44	-	0	-	0	-	0.001	-
2	"	-	2.02	-	38.9	2.51	"	4.76
3	"	24.55	5.99	30.54	77.9	4.37	"	5.00
4	"	20.22	10.30	30.52	116.8	6.14	"	5.18
5	"	16.16	14.23	30.39	155.8	7.97	"	5.28
6	"	9.95	20.38	30.33	233.6	12.2	"	5.48
7	"	6.29	24.04	30.33	311.5	16.2	"	5.57
8	"	4.16	26.13	30.29	390.7	21.1	"	5.75
9	"	1.90	-	-	585.8	32.9	"	5.97
10	"	1.08	-	-	781.4	44.8	"	6.08
11	"	0.693	-	-	976.5	56.8	"	6.23
12	"	0.331	-	-	1563.	93.5	"	6.40

* 1391 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE XLV B

Distribution ratio (D), percent extraction (E), and molar concentrations (M) for zinc pyridine thiocyanate extractions*

Ext. No.	Zinc				Pyridine		Thiocyanate***	
	Found, M x 10^3				Found, M x 10^3		Found, M x 10^3	
	H_2O	$CHCl_3$	D	E	H_2O	$CHCl_3$**	H_2O	$CHCl_3$
1	5.10**	0	0	0	-	-	262.8	0
2	4.77**	0.351	0.0737	6.63	0.348	5.24	262.0	0.702
3	4.12	1.04	0.253	19.6	0.607	10.6	260.8	2.08
4	3.40	1.79	0.527	33.7	0.852	15.9	259.4	3.58
5	2.72	2.47	0.908	46.7	1.11	21.2	258.4	4.94
6	1.67	3.54	2.12	67.5	1.69	31.8	256.3	7.08
7	1.06	4.18	3.94	79.5	2.25	42.4	255.2	8.36
8	0.700	4.53	6.48	86.4	2.93	53.0	254.8	9.06
9	0.321	4.94**	15.4	93.8	4.59	79.1	254.5	9.88
10	0.183	5.07**	27.7	96.2	6.26	105.	255.0	10.1
11	0.117	5.12**	43.8	97.8	7.97	131.	255.3	10.2
12	0.0566	5.15**	91.0	98.9	13.2	208.	256.8	10.3

* Basic data are in Table XLV A.

** Calculated by difference.

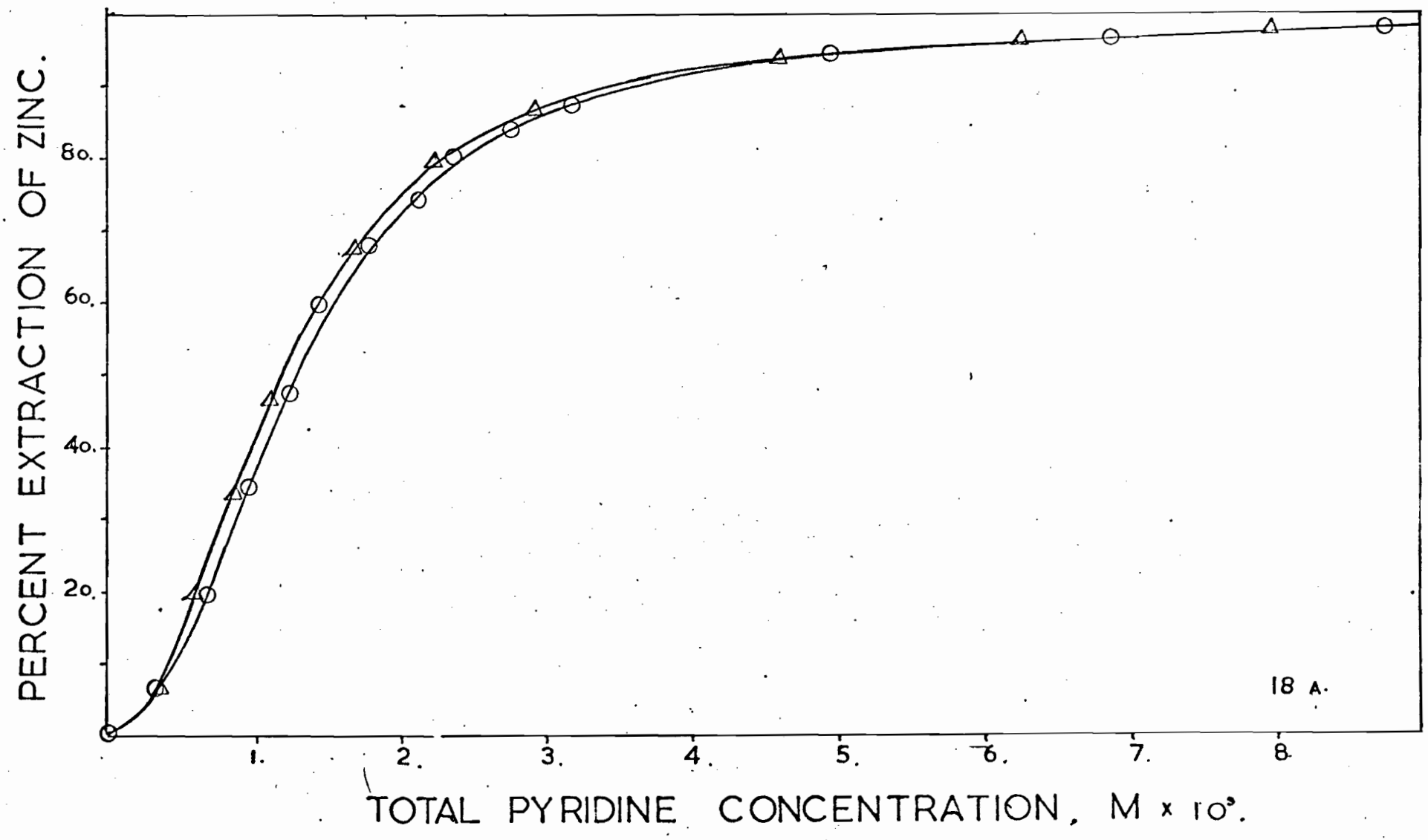
*** The molar ratio of thiocyanate to zinc in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known zinc concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

FIGURES 18A AND 18B

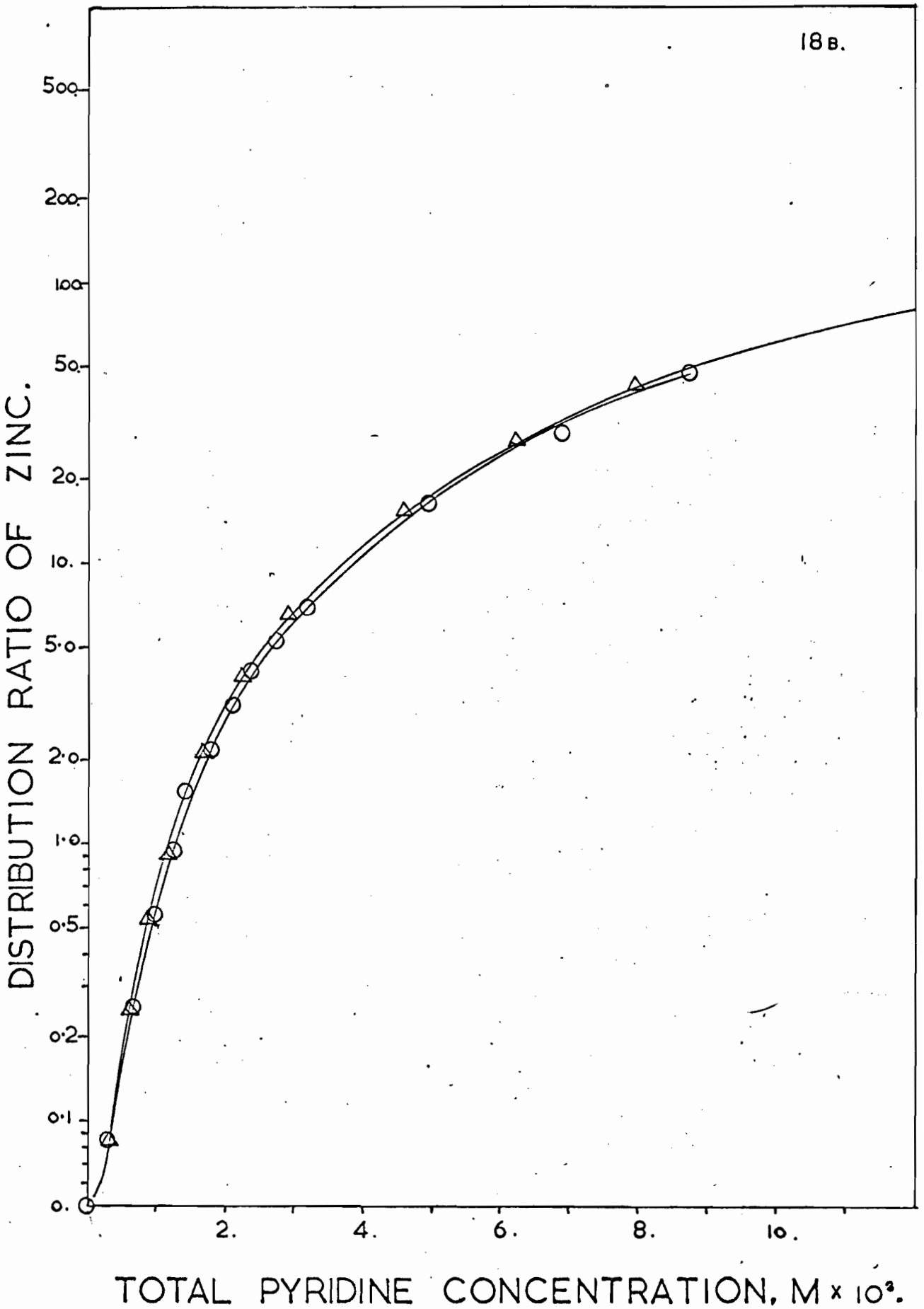
Extraction of zinc pyridine thiocyanate into chloroform, as a function of the total equilibrium concentration of pyridine in the aqueous phase; effect of 0.001-M pyridinium chloride on the percent extraction (18A) and on the distribution ratio (18B).

⊙ = pyridinium chloride absent.

△ = pyridinium chloride present.


PERCENT EXTRACTION OF ZINC.
80.
60.
40.
20.
1.
2.
3.
4.
5.
6.
7.
8.
TOTAL PYRIDINE CONCENTRATION, M x 10⁵.
18 A.

18B.


DISTRIBUTION RATIO OF ZINC.
500
200
100
50
20
10.
5.0
2.0
1.0
0.5
0.2
0.1
0.
2.
4.
6.
8.
10.
TOTAL PYRIDINE CONCENTRATION, M x 10³.

librium concentration of pyridine. The results are in Tables XLVI and XLVII. The plots of E and D against the total equilibrium concentration of pyridine in the aqueous phase are shown in Figs. 19A and 19B, respectively. It was evident that the presence of pyridinium chloride resulted in a small, but statistically-significant* displacement of the extraction curve to the left. This was the same effect noticed in nickel, cobalt and zinc pyridine thiocyanate extraction systems**.

Although not determined experimentally, it was expected that a reduction of the initial concentration of cadmium in the extraction system would result, as for nickel and cobalt pyridine thiocyanate systems, in a small displacement of the extraction curve to the left.

4-5. Cobalt 2-Picoline, 3-Picoline and 4-Picoline Thiocyanates

The distribution of cobalt 2-picoline thiocyanate between chloroform and aqueous solutions of 0.3-M thiocyanate was studied as a function of the equilibrium concentration of 2-picoline. The results are in Table XLVIII. The plots of E and D against the total equilibrium concentration of 2-picoline in the aqueous phase are shown in Figs. 20A and 20B, respectively. This system was not studied in the presence of 2-picolinium chloride.

The distribution of cobalt 3-picoline thiocyanate between chloroform and aqueous solutions of 0.3-M thiocyanate was studied, both in the presence and in the absence of 3-picolinium chloride, as a function of the

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* See *, page 125.

** See Parts V-4-1, 2 and 3, respectively, for details.

TABLE XLVI A

Effect of the pyridine concentration on the distribution of cadmium between chloroform and aqueous thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cadmium				Pyridine		Thiocyanate		Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O	Taken, mg (in H_2O)	Found, mg $CHCl_3$	
1	12.86	-	0	-	0	-	1389	-	-
2	"	12.50	0.303	12.80	197.2	13.8	"	0.50	7.07
3	"	11.47	1.21	12.68	294.5	20.4	"	1.39	7.13
4	"	9.77	3.16	12.93	394.5	26.1	"	3.50	7.20
5	"	7.42	5.32	12.74	490.8	31.5	"	5.86	7.13
6R	"	5.34	7.56	12.90	591.7	37.7	"	8.02	7.30
7	"	3.54	9.04	12.58	687.1	43.3	"	9.40	7.32
8	"	2.42	10.35	12.77	789.0	50.0	"	11.0	7.36
9	"	1.56	11.01	12.57	883.4	54.9	"	11.8	7.37
10	"	1.31	11.69	13.00	986.2	61.4	"	12.6	7.42
11	"	0.273	12.41	12.68	1374.	84.7	"	13.1	7.49

NOTE: Extraction 6R is the mean of 4 replicates.

TABLE XLVI B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for cadmium pyridine thiocyanate extractions

Ext. No.	Cadmium				Pyridine		Thiocyanate		Molar ratio of thiocyanate to cadmium in $CHCl_3$ phase
	Found, M x 10^3		D	E	Found, M x 10^3		Found, M x 10^3		
	H_2O	$CHCl_3$			H_2O	$CHCl_3$**	H_2O**	$CHCl_3$	
1	1.25**	0	0	0	-	-	-	-	-
2	1.22	0.0306	0.0251	2.36	1.92	26.4	262.7	0.0980	3.20
3	1.12	0.122	0.109	9.54	2.83	38.9	262.6	0.272	2.23
4	0.957	0.318	0.332	24.6	3.63	52.8	262.6	0.684	2.15
5	0.728	0.536	0.737	41.8	4.39	65.8	262.5	1.14	2.13
6R	0.524	0.761	1.45	58.6	5.26	79.3	262.4	1.56	2.05
7	0.348	0.909	2.61	71.7	6.04	92.1	262.4	1.83	2.01
8	0.238	1.04	4.37	80.9	6.99	105.	262.3	2.14	2.06
9	0.154	1.10	7.15	87.4	7.68	118.	262.5	2.29	2.07
10	0.129	1.17	9.07	89.8	8.61	132.	262.6	2.44	2.08
11	0.0270	1.24	45.9	97.9	11.9	183.	263.5	2.53	2.04

* Basic data are in Table XLVI A.

** Calculated by difference.

TABLE XLVII A

Effect of pyridine, in the presence of pyridinium chloride, on the distribution of cadmium between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cadmium				Pyridine		Pyridinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	12.86	-	0	-	0	-	0.001	-
2	"	12.70	0.240	12.84	195.4	12.7	"	5.22
3	"	11.51	1.18	12.69	293.1	18.9	"	5.73
4	"	9.70	3.08	12.78	390.7	25.1	"	5.82
5	"	7.42	5.35	12.77	488.4	30.9	"	5.93
6	"	5.35	7.52	12.77	586.1	36.7	"	5.97
7	"	3.72	9.15	12.87	683.8	42.4	"	6.07
8	"	2.43	10.33	12.76	781.4	48.2	"	6.11
9	"	1.47	11.10	12.57	879.1	54.7	"	6.20
10	"	1.01	11.60	12.86	976.8	60.3	"	6.22
11	"	0.228	-	-	1368.	83.2	"	6.39
12	"	0.113	-	-	1758.	108.	"	6.47

* 1391 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE XLVII B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for cadmium pyridine thiocyanate extractions*

Ext. No.	Cadmium				Pyridine		Thiocyanate***	
	Found, M x 10^3		D	E	Found, M x 10^3		Found, M x 10^3	
	H_2O	$CHCl_3$			H_2O	$CHCl_3$**	H_2O	$CHCl_3$
1	1.25**	0	0	0	-	-	262.5	0
2	1.24	0.0243	0.0196	1.86	1.76	26.2	263.2	0.0486
3	1.13	0.119	0.105	9.24	2.63	39.4	263.2	0.238
4	0.950	0.311	0.327	24.1	3.50	52.5	263.0	0.622
5	0.728	0.540	0.742	41.9	4.30	65.4	263.0	1.08
6	0.525	0.757	1.44	58.4	5.12	78.5	262.8	1.64
7	0.366	0.920	2.51	71.1	5.92	91.6	262.7	1.84
8	0.239	1.04	4.35	81.0	6.75	105.	263.0	2.08
9	0.145	1.11	7.66	88.3	7.65	117.	263.0	2.22
10	0.0992	1.16	11.7	92.0	8.44	130.	263.3	2.32
11	0.0226	1.26**	55.8	98.3	11.7	182.	264.2	2.52
12	0.0112	1.27**	113.	99.1	15.3	233.	265.3	2.54

* Basic data are in Table XLVII A.

** Calculated by difference.

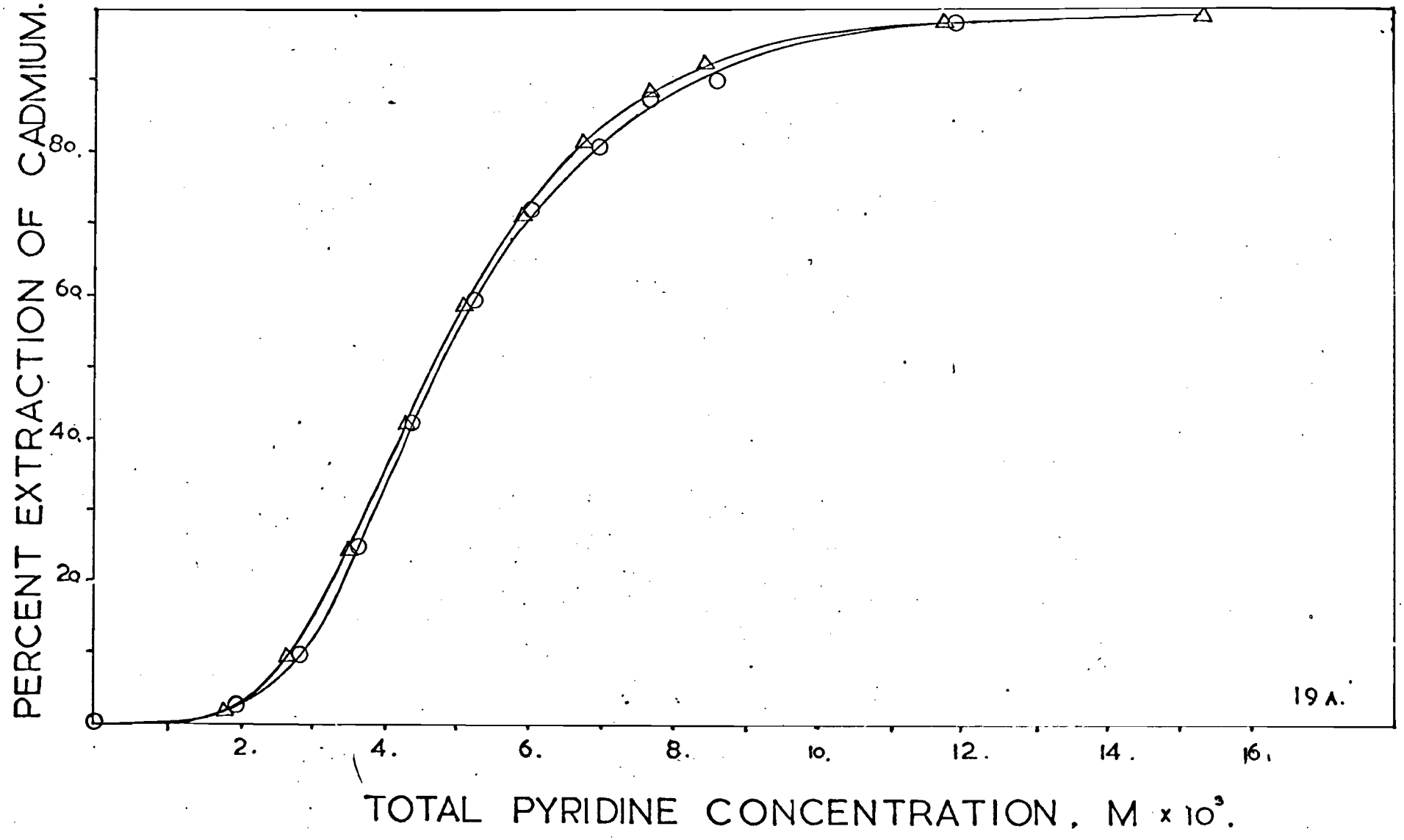
*** The molar ratio of thiocyanate to cadmium in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known cadmium concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

FIGURES 19A AND 19B

Extraction of cadmium pyridine thiocyanate into chloroform, as a function of the total equilibrium concentration of pyridine in the aqueous phase; effect of 0.001-M pyridinium chloride on the percent extraction (19A) and on the distribution ratio (19B).

⊙ = pyridinium chloride absent.

△ = pyridinium chloride present.


PERCENT EXTRACTION OF CADMIUM.
80.
60.
40.
20.
2.
4.
6.
8.
10.
12.
14.
16.
19 A.
TOTAL PYRIDINE CONCENTRATION, M x 10³.

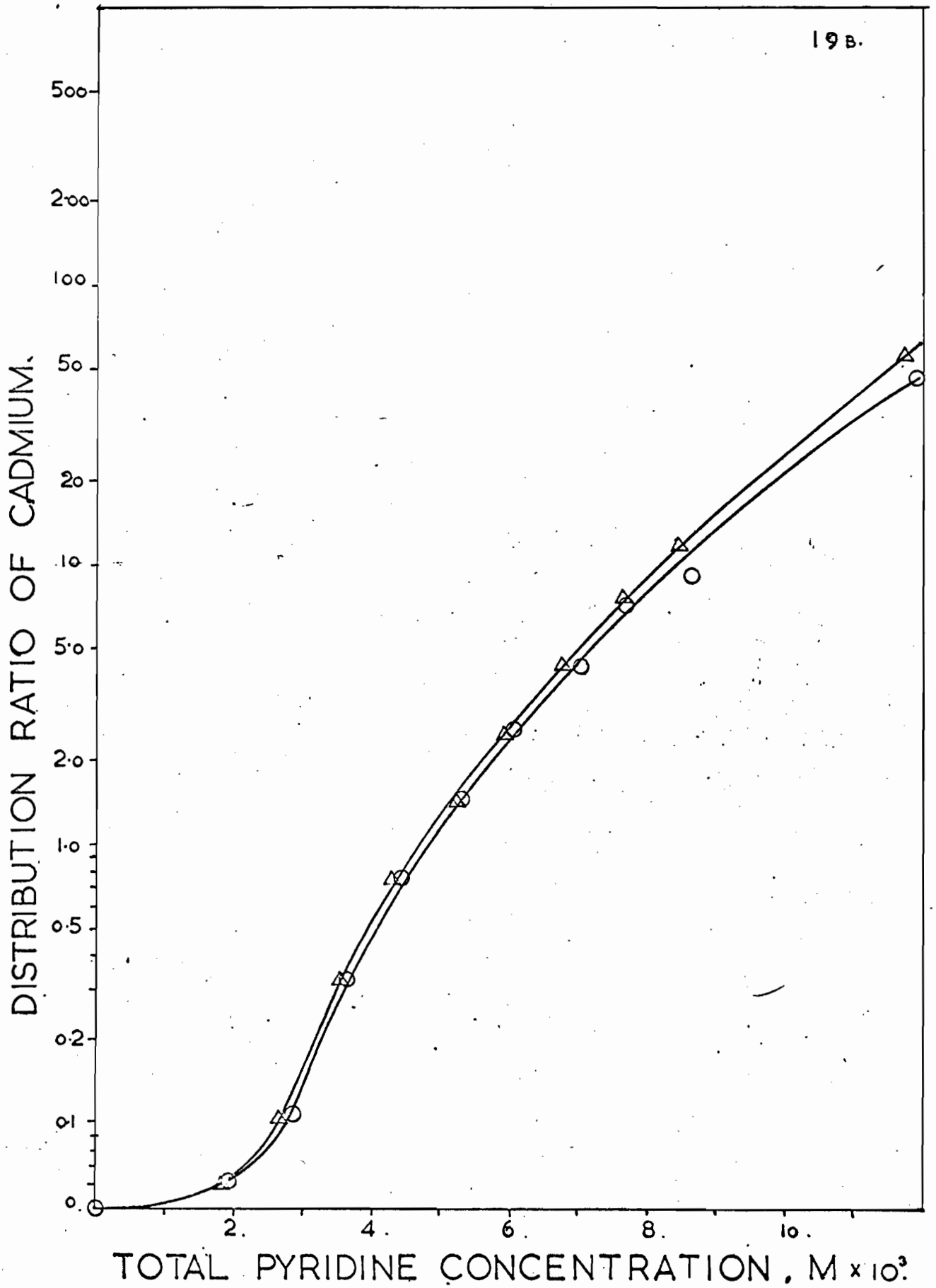

19B.
DISTRIBUTION RATIO OF CADMIUM.
500
200
100
50
20
10
5·0
2·0
1·0
0·5
0·2
0·1
0.
2.
4.
6.
8.
10.
TOTAL PYRIDINE CONCENTRATION, M x 10³.

TABLE XLVIII A

Effect of the 2-picoline concentration on the distribution of cobalt between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cobalt				2-Picoline		Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O	
1	13.84	-	0	-	0	0	-
2	"	13.61	0.211	13.82	1378	31.9	7.54
3R	"	12.73	1.05	13.78	3261	76.8	8.03
4	"	11.62	1.94	13.56	4490	104.	8.10
5	"	9.97	4.05	14.02	6889	155.	8.20
6	"	7.91	6.05	13.96	8984	201.	8.40
7	"	5.96	7.98	13.94	11480	254.	8.47
8	"	4.69	9.19	13.88	13480	300.	8.60
9	"	3.39	10.60	13.89	16070	359.	8.60
10	"	2.71	11.03	13.74	17970	400.	8.66
11	"	1.63	11.95	13.57	22460	498.	8.77
12	"	0.515	13.30	13.82	33260	691.	8.74
13	"	0.123	13.53	13.65	47500	829.	8.88

* 1387 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

NOTE: Extraction 3R is the mean of 4 replicates.

TABLE XLVIII B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for cobalt 2-picoline thiocyanate extractions*

Ext. No.	Cobalt				2-Picoline		Thiocyanate***	
	Found, M x 10^3		D	E	Found, M x 10^3		Found, M x 10^3	
	H_2O	$CHCl_3$			H_2O	$CHCl_3$**	H_2O	$CHCl_3$
1	2.58**	0	0	0	0	0	261.8	0
2	2.57	0.0401	0.0156	1.52	3.82	162.	265.8	0.080
3R	2.46	0.196	0.0797	7.63	9.39	376.	271.3	0.39
4	2.27	0.357	0.157	14.3	12.9	511.	274.2	0.71
5	2.01	0.724	0.360	28.9	19.8	763.	282.3	1.45
6	1.64	1.06	0.646	43.3	26.3	973.	288.6	2.12
7	1.27	1.36	1.07	57.3	34.3	1210.	297.0	2.76
8	1.03	1.53	1.49	66.1	41.6	1390.	304.5	3.06
9	0.770	1.72	2.23	75.7	51.6	1620.	314.7	3.44
10	0.633	1.76	2.78	80.2	59.1	1780.	323.3	3.52
11	0.406	1.83	4.51	88.0	78.4	2090.	344.0	3.66
12	0.154	1.85	12.0	96.2	130.	2870.	410.3	3.70
13	0.0492	1.68	34.2	99.2	476.	3670.	551.5	3.36

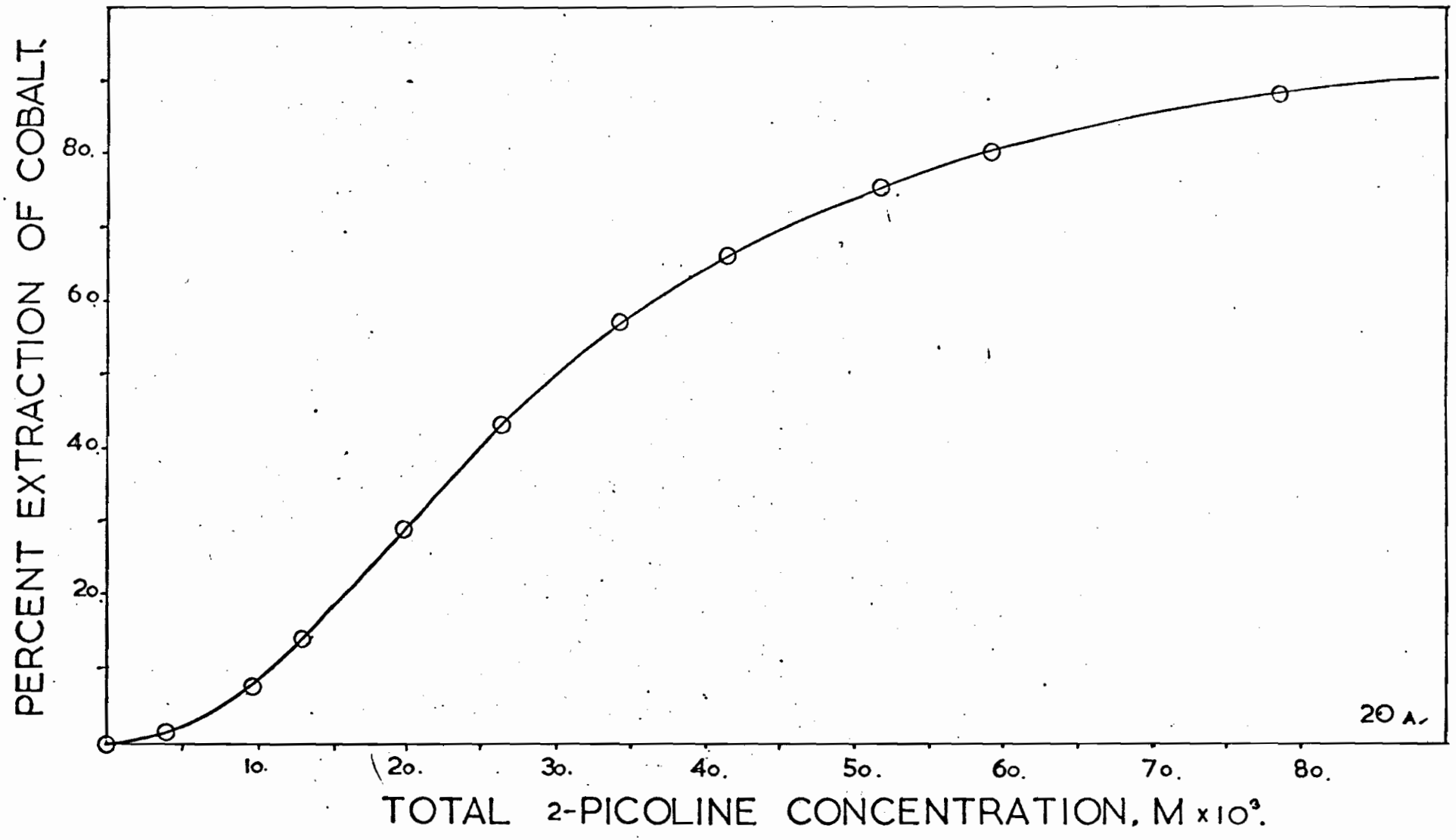
* Basic data are in Table XLVIII A.

** Calculated by difference.

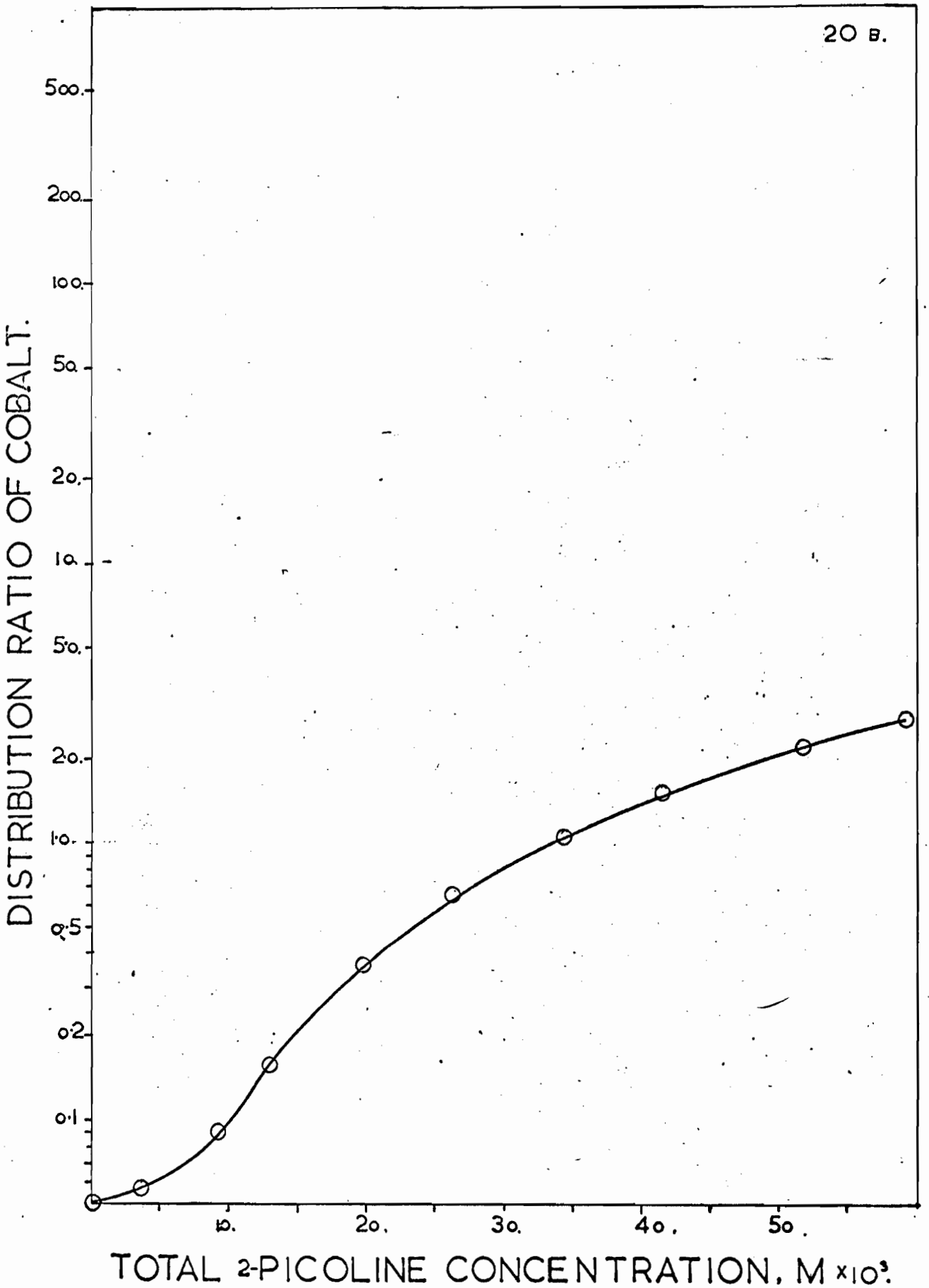
*** The molar ratio of thiocyanate to cobalt in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known cobalt concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

FIGURES 20A AND 20B

Extraction of cobalt 2-picoline thiocyanate into chloroform, as a function of the total equilibrium concentration of 2-picoline in the aqueous phase; effect on the percent extraction (20A) and on the distribution ratio (20B).


PERCENT EXTRACTION OF COBALT.
80.
60.
40.
20.
10.
20.
30.
40.
50.
60.
70.
80.
TOTAL 2-PICOLINE CONCENTRATION, M x 10³.
20 A.

20 B.


DISTRIBUTION RATIO OF COBALT.
500.
200.
100.
50.
20.
10.
5.0.
2.0.
1.0.
0.5
0.2
0.1
10.
20.
30.
40.
50.
TOTAL 2-PICOLINE CONCENTRATION, M x10³.

equilibrium concentration of 3-picoline. The results are in Tables XLIX and L. The results of similar extractions that were carried out by using 4-picoline, rather than 3-picoline, are in Tables LI and LII. The plots of E and D against the total equilibrium concentration of the picoline in the aqueous phases are shown in Figs. 21A and 21B, respectively. For both of these extraction systems, it was evident that the presence of the corresponding picolinium chloride resulted in a small, but statistically-significant* displacement of the extraction curve to the left. This was the same effect noticed in each of the metal pyridine thiocyanate extraction systems**.

4-6. Nickel 3-Picoline and 4-Picoline Thiocyanates

The distribution of nickel 3-picoline thiocyanate between chloroform and aqueous solutions of 0.3-M thiocyanate was studied, in the presence of 3-picolinium chloride, as a function of the equilibrium concentration of 3-picoline. The results are in Table LIII. The results of similar extractions that were carried out by using 4-picoline, rather than 3-picoline, are in Table LIV. The plots of E and D against the total equilibrium concentration of the picoline in the aqueous phase are shown in Figs. 22A and 22B, respectively.

4-7. Zinc 3-Picoline and 4-Picoline Thiocyanates

The distribution of zinc 3-picoline thiocyanate between chloroform and aqueous solutions of 0.3-M thiocyanate was studied, in the

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* See *, page 125.

** See Parts V-4-1, 2, 3 and 4 for details.

TABLE XLIX A

Effect of the 3-picoline concentration on the distribution of cobalt between chloroform and aqueous thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cobalt				3-Picoline		Thiocyanate		Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O	Taken, mg (in H_2O)	Found, mg $CHCl_3$	
1	13.80	-	0	-	0	-	1387	-	-
2	"	-	0.168	-	118.8	2.67	"	-	6.43
3	"	12.10	1.69	13.79	237.6	4.59	"	3.59	6.54
4	"	-	3.92	-	320.7	6.11	"	-	6.76
5	"	-	6.36	-	404.	7.38	"	-	6.78
6R	"	5.51	8.22	13.73	475.	7.73	"	16.8	6.72
7	"	3.11	-	-	594.	10.1	"	-	6.80
8	"	1.68	11.99	13.66	713.	11.3	"	24.2	6.83
9	"	0.936	-	-	831.	14.0	"	-	6.88
10	"	0.549	13.26	13.81	950.	16.5	"	26.7	7.03
11	"	0.159	-	-	1306.	22.8	"	-	7.10

NOTE: Extraction 6R is the mean of 4 replicates.

TABLE XLIX B

Distribution ratio (D), percent extraction (E) and molar concentrations (M), for cobalt 3-picoline thiocyanate extractions*

Ext. No.	Cobalt				3-Picoline		Thiocyanate		Molar ratio of thiocyanate to cobalt in $CHCl_3$ phase
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O**	$CHCl_3$	
1	2.57**	0	0	0	-	-	-	-	
2	2.54**	0.0325	0.0128	1.22	0.315	14.2	-	-	
3	2.26	0.326	0.144	12.24	0.542	27.4	261.8	0.702	2.15
4	1.84**	0.755	0.410	28.4	0.722	38.4	-	-	
5	1.39**	1.22	0.878	46.0	0.873	48.3	-	-	
6R	1.03	1.58	1.53	60.0	0.914	56.9	259.7	3.27	2.07
7	0.582	2.06**	3.54	77.4	1.20	71.0	-	-	
8	0.315	2.30	7.31	87.7	1.34	85.2	259.2	4.71	2.05
9	0.176	2.46**	14.0	93.2	1.66	100.	-	-	
10	0.103	2.54	24.7	96.2	1.97	113.	259.3	5.18	2.04
11	0.0300	2.60**	86.7	98.9	2.72	155.	-	-	

* Basic data are in Table XLIX A.

** Calculated by difference.

TABLE L A

Effect of the 3-picoline concentration, in the presence of 3-picolinium chloride, on the distribution of cobalt between chloroform and aqueous thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cobalt				3-Picoline		Thiocyanate		3-Picolinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O	Taken, mg (in H_2O)	Found, mg $CHCl_3$		
1	13.80	-	0	-	0	-	1387	-	0.001	-
2	"	-	0.172	-	118.8	2.36	"	-	"	5.25
3	"	-	1.975	-	237.6	4.44	"	4.01	"	5.32
4	"	-	3.95	-	320.7	5.69	"	7.89	"	5.60
5	"	-	6.41	-	404.	6.83	"	12.9	"	5.65
6	"	5.44	8.25	13.69	475.	7.60	"	-	"	5.63
7	"	3.11	-	-	594.	9.77	"	21.8	"	5.82
8	"	0.949	-	-	831.	14.3	"	25.8	"	5.90

TABLE L B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for cobalt 3-picoline thiocyanate extractions*

Ext. No.	Cobalt				3-Picoline		Thiocyanate		Molar ratio of thiocyanate to cobalt in $CHCl_3$ phase
	Found, M x 10^3		D	E	Found, M x 10^3		Found, M x 10^3		
	H_2O	$CHCl_3$			H_2O	$CHCl_3$**	H_2O**	$CHCl_3$	
1	2.57**	0	0	0	-	-	-	-	-
2	2.54**	0.0332	0.0131	1.25	0.278	14.2	-	-	-
3	2.20**	0.381	0.173	14.3	0.524	28.4	261.6	0.784	2.06
4	1.84**	0.761	0.413	28.6	0.672	39.0	261.3	1.54	2.03
5	1.38**	1.23	0.892	46.4	0.808	47.9	260.4	2.51	2.04
6	1.02	1.59	1.56	60.3	0.899	56.9	-	-	-
7	0.582	2.05**	3.52	77.4	1.16	71.1	259.2	4.24	2.07
8	0.178	2.46**	13.8	93.3	1.69	98.9	259.2	5.01	2.04

* Basic data are in Table L A.

** Calculated by difference.

TABLE LI A

Effect of the 4-picoline concentration on the distribution of cobalt between chloroform and aqueous thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cobalt				4-Picoline		Thiocyanate		Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O	Taken, mg (in H_2O)	Found, mg $CHCl_3$	
1	13.84	-	0	-	0	-	1391	-	-
2	"	-	0.270	-	75.9	1.93	"	0.77	6.70
3	"	11.92	1.97	13.89	142.3	3.15	"	4.02	6.50
4	"	-	4.03	-	189.8	3.99	"	8.20	6.91
5	"	-	6.31	-	237.3	4.67	"	12.7	7.00
6R	"	5.49	8.24	13.73	284.6	5.24	"	16.5	6.74
7	"	3.19	-	-	351.0	6.32	"	-	7.08
8	"	1.65	12.16	13.81	426.9	7.73	"	24.5	6.80
9	"	0.897	-	-	493.0	8.92	"	-	7.20
10	"	0.510	13.20	13.71	569.0	10.3	"	26.6	7.02
11	"	0.0427	-	-	1044	20.1	"	-	7.45

NOTE: Extraction 6R is the mean of 4 replicates.

TABLE LI B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for cobalt 4-picoline thiocyanate extractions*

Ext. No.	Cobalt				4-Picoline		Thiocyanate		Molar ratio of thiocyanate to cobalt in $CHCl_3$ phase
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O**	$CHCl_3$	
1	2.58**	0	0	0	-	-	-	-	-
2	2.52**	0.0521	0.0207	1.96	0.228	11.1	262.8	0.151	2.90
3	2.22	0.380	0.171	13.5	0.372	17.0	262.2	0.788	2.07
4	1.83**	0.777	0.425	29.1	0.471	22.7	261.7	1.60	2.06
5	1.40**	1.22	0.872	45.7	0.552	28.4	260.9	2.48	2.03
6R	1.02	1.59	1.56	60.3	0.619	34.1	260.4	3.23	2.03
7	0.596	2.05**	3.44	77.0	0.748	42.0	-	-	-
8	0.310	2.34	7.56	88.0	0.915	51.0	259.4	4.78	2.04
9	0.168	2.49**	14.8	93.5	1.06	58.9	-	-	-
10	0.0955	2.53	26.5	96.3	1.22	68.0	259.2	5.18	2.05
11	0.00805	2.63**	327	99.8	2.40	124.	-	-	-

* Basic data are in Table LI A.

** Calculated by difference.

TABLE LII A

Effect of the 4-picoline concentration, in the presence of 4-picolinium chloride, on the distribution of cobalt between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cobalt				4-Picoline		4-Picolinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	13.84	-	0	-	0	-	0.001	-
2	"	-	0.278	-	75.9	1.56	"	5.34
3	"	-	2.04	-	142.4	2.61	"	5.65
4	"	-	4.08	-	189.8	3.70	"	5.80
5	"	-	6.26	-	237.3	4.16	"	5.87
6	"	5.66	8.10	13.76	284.6	4.91	"	5.54
7	"	3.18	-	-	351.0	5.66	"	6.05
8	"	0.923	-	-	493.0	8.61	"	6.12

* 1391 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE LII B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for cobalt 4-picoline thiocyanate extractions*

Ext. No.	Cobalt				4-Picoline		Thiocyanate***	
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O	$CHCl_3$
1	2.57**	0	0	0	-	-	262.6	0
2	2.53**	0.0535	0.0212	2.01	0.184	9.09	262.7	0.107
3	2.20**	0.394	0.179	14.7	0.308	17.1	262.0	0.788
4	1.82**	0.787	0.432	29.5	0.437	22.7	261.6	1.57
5	1.41**	1.21	0.858	45.3	0.492	28.4	261.0	2.42
6	1.06	1.56	1.47	58.8	0.580	34.2	260.4	3.12
7	0.594	2.05**	3.45	77.0	0.670	42.0	259.6	4.10
8	0.173	2.48**	14.3	93.5	1.02	58.9	259.2	4.96

* Basic data are in Table LII A.

** Calculated by difference.

*** The molar ratio of thiocyanate to cobalt in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known cobalt concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

FIGURES 21A AND 21B

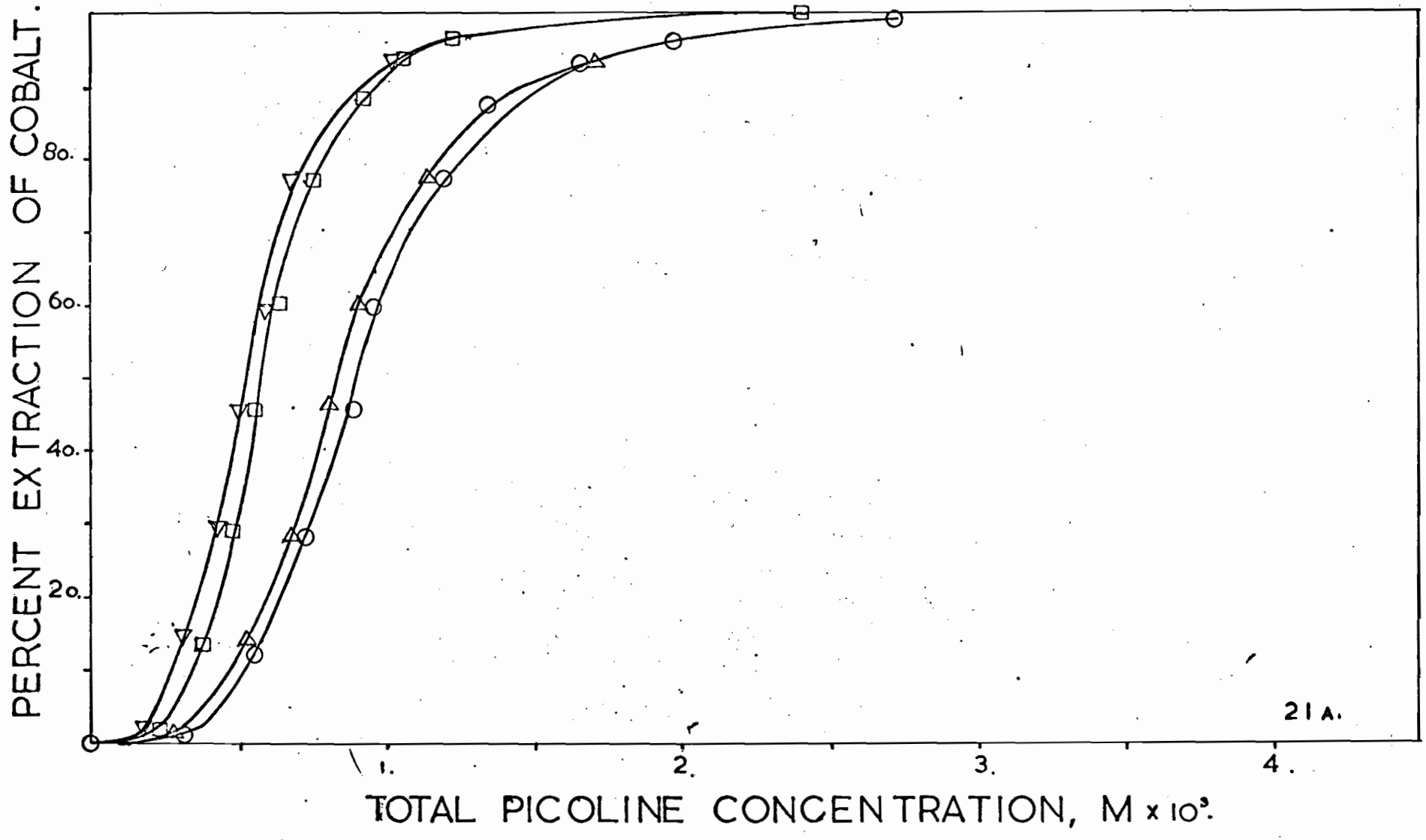
Extraction of cobalt 3-picoline and 4-picoline thiocyanates into chloroform, as a function of the total equilibrium concentration of the picoline in the aqueous phase; effect of 0.001-M picolinium chloride on the percent extraction (21A) and on the distribution ratio (21B).

⊙ = 3-picoline extractions.

△ = 3-picoline extractions in the presence of 3-picolinium chloride.

⊡ = 4-picoline extractions.

▽ = 4-picoline extractions in the presence of 4-picolinium chloride.


PERCENT EXTRACTION OF COBALT.
80.
60.
40.
20.
1.
2.
3.
4.
TOTAL PICOLINE CONCENTRATION, M x 10³.
21 A.

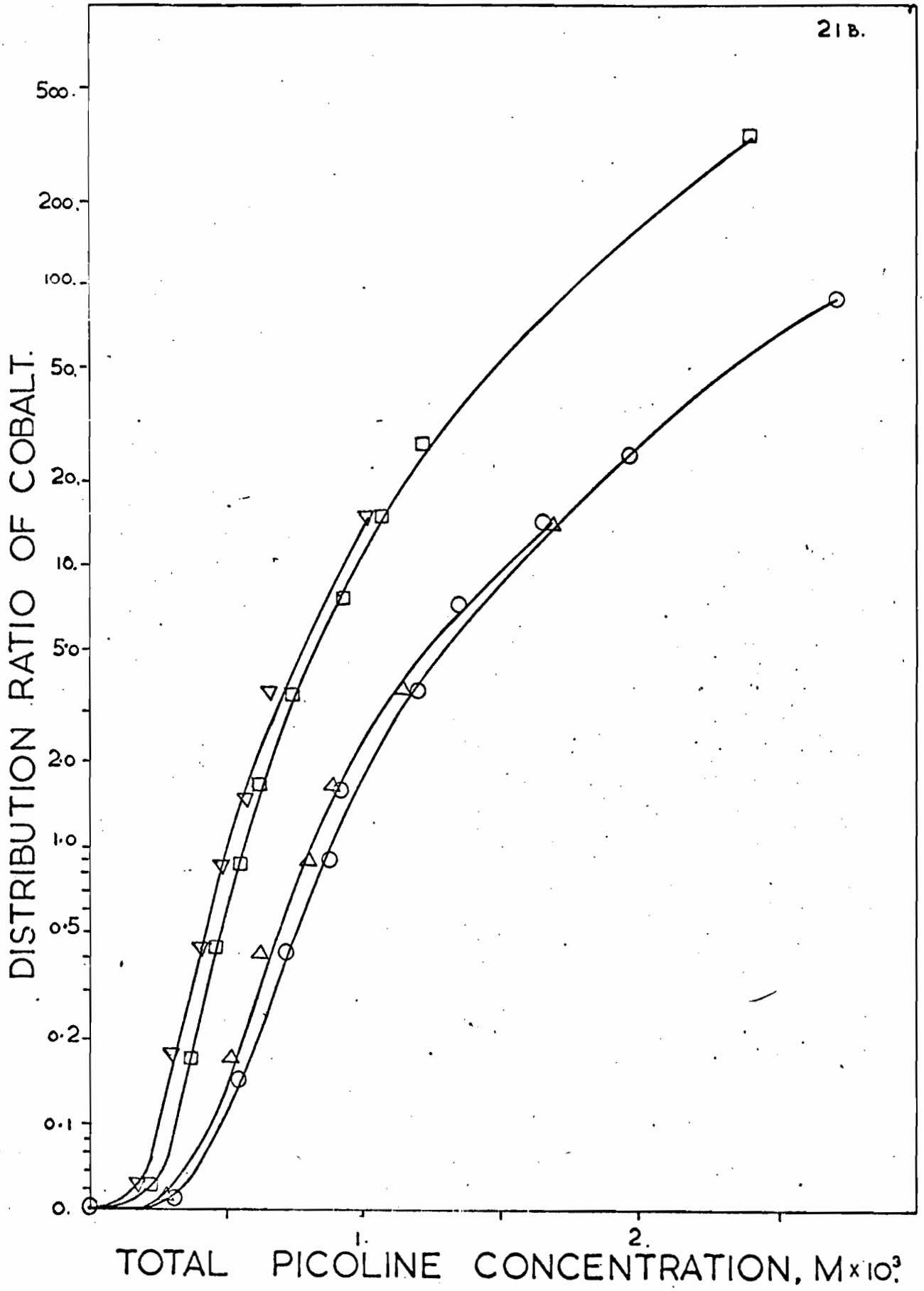

21 B.
500.
200.
100.
50.
20.
10.
5·0
2·0
1·0
0·5
0·2
0·1
0.
DISTRIBUTION RATIO OF COBALT.
1.
2.
TOTAL PICOLINE CONCENTRATION, M x 10³.

TABLE LIII A

Effect of the 3-picoline concentration, in the presence of 3-picolinium chloride, on the distribution of nickel between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Nickel				3-Picoline		3-Picolinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	27.40	-	0	-	0	-	0.001	-
2	"	-	1.13	-	47.4	0.868	"	4.68
3	"	-	5.18	-	94.9	1.39	"	4.88
4	"	-	9.92	-	142.3	1.95	"	5.00
5	"	-	13.90	-	189.9	2.31	"	5.08
6	"	8.33	-	-	237.2	2.43	"	5.16
7	"	4.84	-	-	284.8	2.77	"	5.38
8	"	1.22	-	-	379.7	3.63	"	5.44
9	"	0.370	-	-	474.6	5.42	"	5.60

* 1395 mg of thiocyanate were taken.
Neither phase was analysed for thiocyanate.

TABLE LIII B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for nickel 3-picoline thiocyanate extractions*

Ext. No.	Nickel				3-Picoline		Thiocyanate***	
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O	$CHCl_3$
1	5.12**	0	0	0	-	-	263.2	0
2	4.91**	0.219	0.0446	4.12	0.102	5.58	263.0	0.44
3	4.15**	1.00	0.241	18.9	0.154	11.4	261.7	2.00
4	3.27**	1.92	0.587	36.2	0.230	17.1	259.7	3.84
5	2.53**	2.69	1.06	50.7	0.273	22.9	258.7	5.38
6	1.56	3.69**	2.36	69.6	0.287	28.7	256.7	7.38
7	0.907	4.36**	4.81	82.4	0.327	34.4	255.7	8.72
8	0.229	5.06**	22.1	95.6	0.430	45.8	254.6	10.1
9	0.0695	5.22**	75.2	98.8	0.642	57.1	254.4	10.4

* Basic data are in Table LIII A.

** Calculated by difference.

*** The molar ratio of thiocyanate to nickel in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from that ratio and the known nickel concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

TABLE LIV A

Effect of the 4-picoline concentration, in the presence of 4-picolinium chloride, on the distribution of nickel between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Nickel				4-Picoline		4-Picolinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	27.40	-	0	-	0	-	0.001	-
2	"	-	3.29	-	47.4	0.842	"	4.95
3	"	-	7.98	-	94.9	1.13	"	5.07
4	"	-	14.15	-	142.3	1.25	"	5.23
5	"	7.75	-	-	189.8	1.51	"	5.30
6	"	3.27	-	-	237.1	1.94	"	5.43
7	"	1.02	-	-	284.7	2.33	"	5.55
8	"	0.149	-	-	379.6	3.94	"	5.78
9	"	0.087	-	-	474.5	5.99	"	5.98

* 1395 mg of thiocyanate were taken.
Neither phase was analysed for thiocyanate.

TABLE LIV B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for nickel 4-picoline thiocyanate extractions*

Ext. No.	Nickel				4-Picoline		Thiocyanate***	
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O	$CHCl_3$
1	5.12**	0	0	0	-	-	263.2	0
2	4.50**	0.638	0.142	12.0	0.0992	5.70	262.3	1.28
3	3.63**	1.55	0.427	29.2	0.133	11.5	260.5	3.10
4	2.48**	2.74	1.10	51.6	0.147	17.2	258.3	5.48
5	1.45	3.81**	2.63	71.9	0.178	23.0	256.3	7.62
6	0.612	4.67**	7.63	88.1	0.229	28.7	254.8	9.34
7	0.191	5.11**	26.8	96.3	0.276	34.4	254.2	10.2
8	0.0280	5.26**	188	99.5	0.466	45.8	254.3	10.5
9	0.0163	5.29**	325	99.7	0.710	57.0	254.4	10.6

* Basic data are in Table LIV A.

** Calculated by difference.

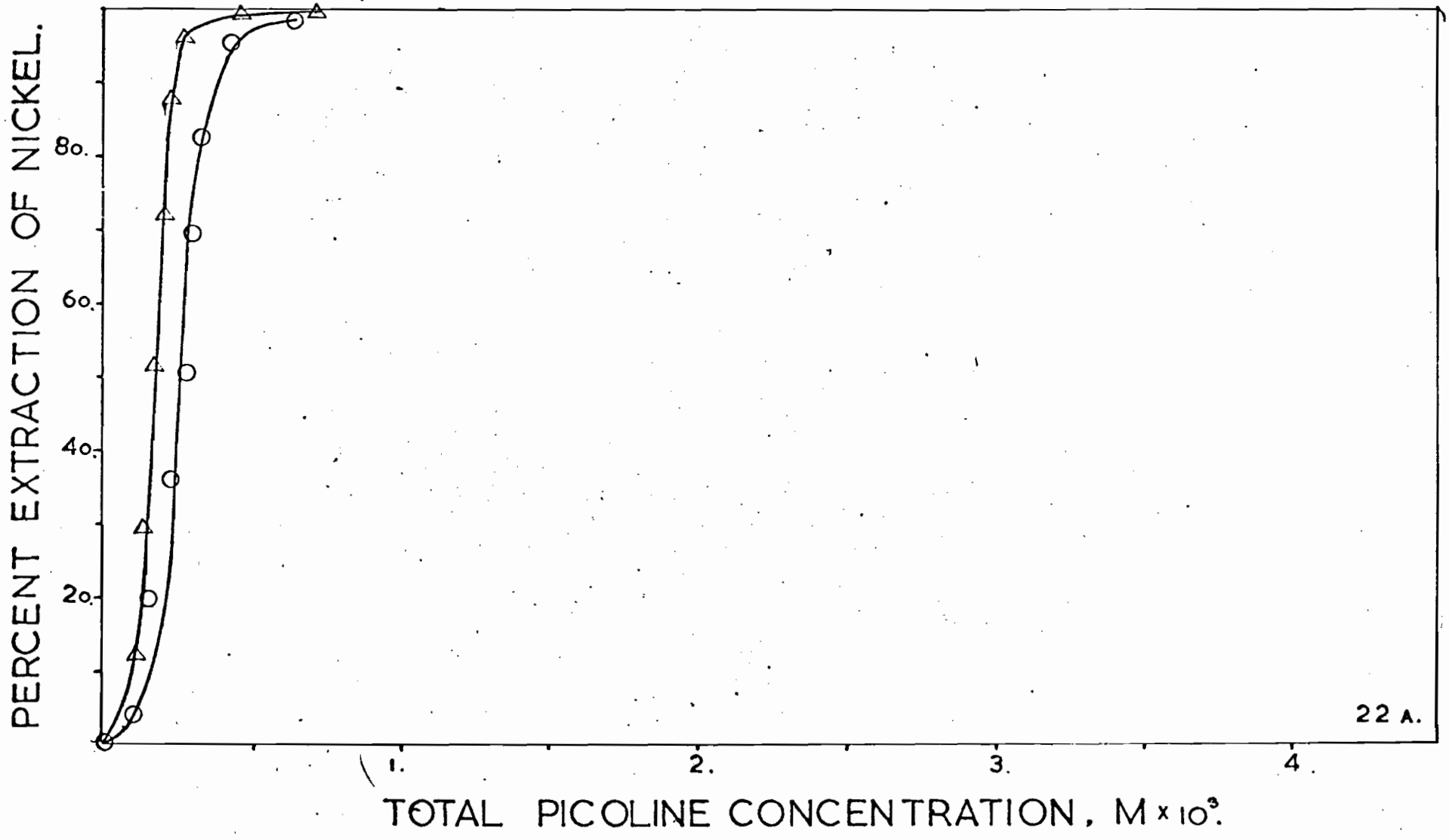
*** The molar ratio of thiocyanate to nickel in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from that ratio and the known nickel concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

FIGURES 22A AND 22B

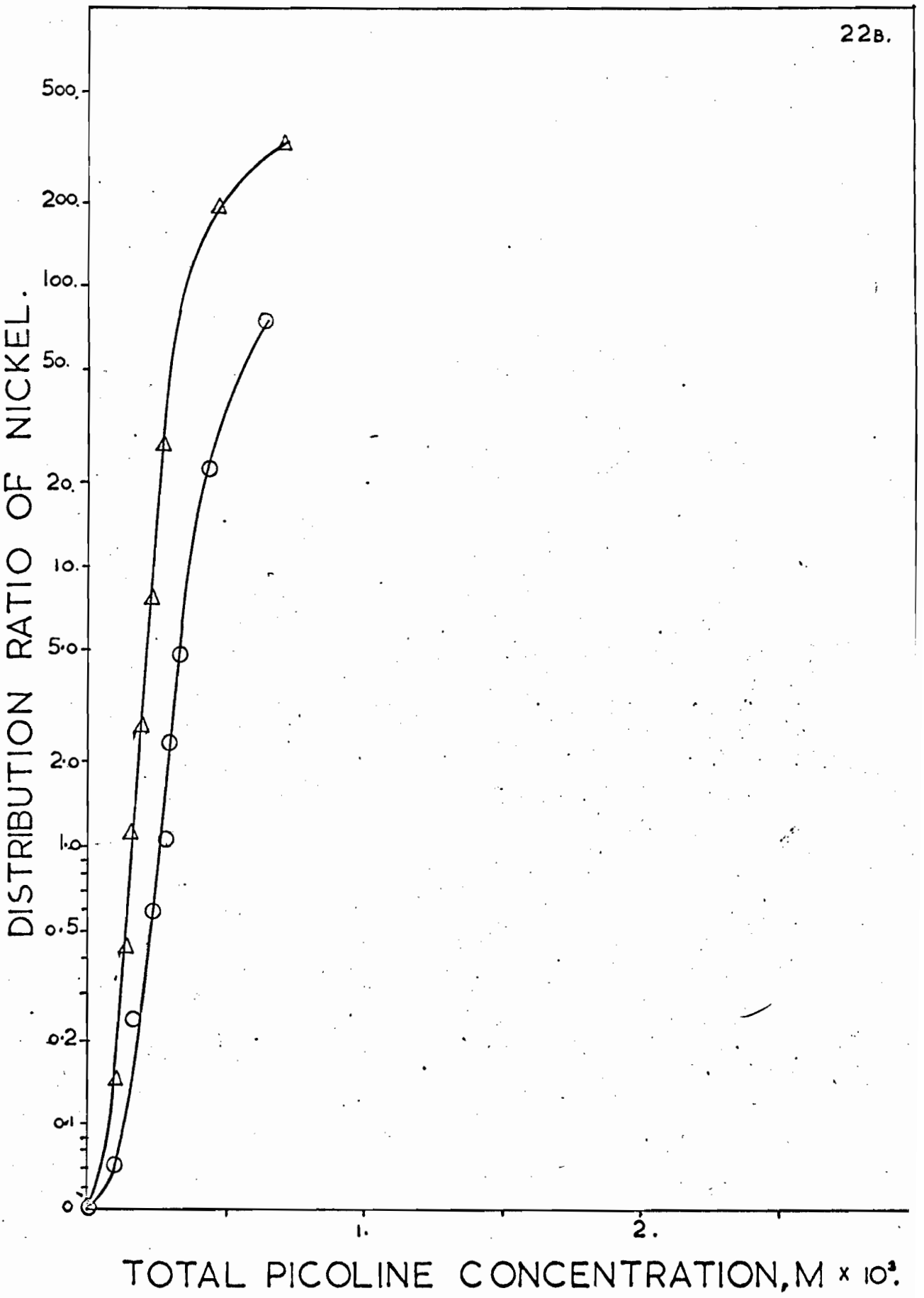
Extraction of nickel 3-picoline and 4-picoline thiocyanates into chloroform, as a function of the total equilibrium concentration of the picoline in the aqueous phase; the percent extraction (22A) and the distribution ratio (22B) in the presence of 0.001-M picolinium chloride.

⊙ = 3-picoline extractions.

△ = 4-picoline extractions.


PERCENT EXTRACTION OF NICKEL.
80.
60.
40.
20.
1.
2.
3.
4.
TOTAL PICOLINE CONCENTRATION, M x 10³.
22 A.

22B.


DISTRIBUTION RATIO OF NICKEL.
500.
200.
100.
50.
20.
10.
5.0
2.0
1.0
0.5
0.2
0.1
0
1.
2.
TOTAL PICOLINE CONCENTRATION, M x 10³.

presence of 3-picolinium chloride, as a function of the equilibrium concentration of 3-picoline. The results are in Table LV. The results of similar extractions that were carried out by using 4-picoline, rather than 3-picoline, are in Table LVI. The plots of E and D against the total equilibrium concentration of the picoline in the aqueous phase are shown in Figs. 23A and 23B, respectively.

4-8. Cadmium 3-Picoline and 4-Picoline Thiocyanates

The distribution of cadmium 3-picoline thiocyanate between chloroform and aqueous solutions of 0.3-M thiocyanate was studied, in the presence of 3-picolinium chloride, as a function of the equilibrium concentration of 3-picoline. The results are in Table LVII. The results of similar extractions that were carried out by using 4-picoline, rather than 3-picoline, are in Table LVIII. The plots of E and D against the total equilibrium concentration of the picoline in the aqueous phase are shown in Figs. 24A and 24B, respectively.

TABLE LV A

Effect of the 3-picoline concentration, in the presence of 3-picolinium chloride, on the distribution of zinc between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Zinc				3-Picoline		3-Picolinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	30.44	-	0	-	0	-	0.001	-
2	"	24.30	6.28	30.58	47.5	0.51	"	4.68
3	"	16.34	14.00	30.34	94.9	0.69	"	4.98
4	"	10.13	20.17	30.30	142.4	1.75	"	5.27
5	"	6.00	24.30	30.30	189.9	2.07	"	5.37
6	"	3.70	26.60	30.30	237.4	3.13	"	5.47
7	"	2.42	27.97	30.39	284.7	3.55	"	5.42
8	"	0.561	29.80	30.36	569.5	8.29	"	5.75
9	"	0.320	30.05	30.37	854	13.24	"	5.95

* 1395 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE LV B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for zinc 3-picoline thiocyanate extractions*

Ext. No.	Zinc				3-Picoline		Thiocyanate***	
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O	$CHCl_3$
1	5.10**	0	0	0	-	-	263.2	0
2	4.07	1.09	0.268	20.5	0.060	5.75	261.3	2.18
3	2.74	2.44	0.891	46.2	0.082	11.5	258.8	4.88
4	1.70	3.51	2.06	66.7	0.206	17.2	256.8	7.02
5	1.01	4.22	4.18	80.3	0.245	22.9	255.7	8.44
6	0.622	4.62	7.43	88.0	0.370	28.6	255.0	9.24
7	0.407	4.86	11.9	92.1	0.420	34.3	254.6	9.72
8	0.0947	5.16	54.5	98.3	0.984	68.2	255.0	10.3
9	0.0542	5.18	95.6	99.0	1.58	102.	256.0	10.4

* Basic data are in Table LV A.

** Calculated by difference.

*** The molar ratio of thiocyanate to zinc in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from that ratio and the known zinc concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

TABLE LVI A

Effect of the 4-picoline concentration, in the presence of 4-picolinium chloride, on the distribution of zinc between chloroform and aqueous thiocyanate* solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Zinc				4-Picoline		4-Picolinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O		
1	30.44	-	0	-	0	-	0.001	-
2	"	21.85	8.55	30.40	47.4	0.35	"	4.98
3	"	12.69	17.61	30.30	94.9	0.91	"	5.41
4	"	6.26	23.85	30.16	142.3	1.46	"	5.53
5	"	3.20	27.08	30.28	189.8	2.51	"	5.71
6	"	1.78	28.42	30.20	237.2	3.21	"	5.83
7	"	1.13	29.22	30.35	284.8	4.05	"	5.77
8	"	0.267	30.05	30.32	569.7	9.59	"	6.14
9	"	0.160	30.06	30.22	854.0	15.30	"	6.33

* 1395 mg of thiocyanate were taken. Neither phase was analysed for thiocyanate.

TABLE LVI B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for zinc 4-picoline thiocyanate extractions*

Ext. No.	Zinc				4-Picoline		Thiocyanate***	
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O	$CHCl_3$
1	5.10**	0	0	0	-	-	263.3.	0
2	3.66	1.49	0.407	28.2	0.043	5.76	260.5	2.98
3	2.13	3.06	1.44	58.3	0.107	10.5	257.7	6.12
4	1.05	4.15	3.95	79.3	0.172	17.2	255.5	8.30
5	0.538	4.70	8.74	89.5	0.293	22.9	254.8	9.40
6	0.299	4.94	16.5	94.3	0.378	28.6	254.4	9.88
7	0.190	5.07	26.7	96.3	0.476	34.2	254.3	10.1
8	0.0451	5.19	115	99.1	1.14	68.0	255.3	10.4
9	0.0271	5.18	191	99.5	1.82	101.	256.2	10.4

* Basic data are in Table LVI A.

** Calculated by difference.

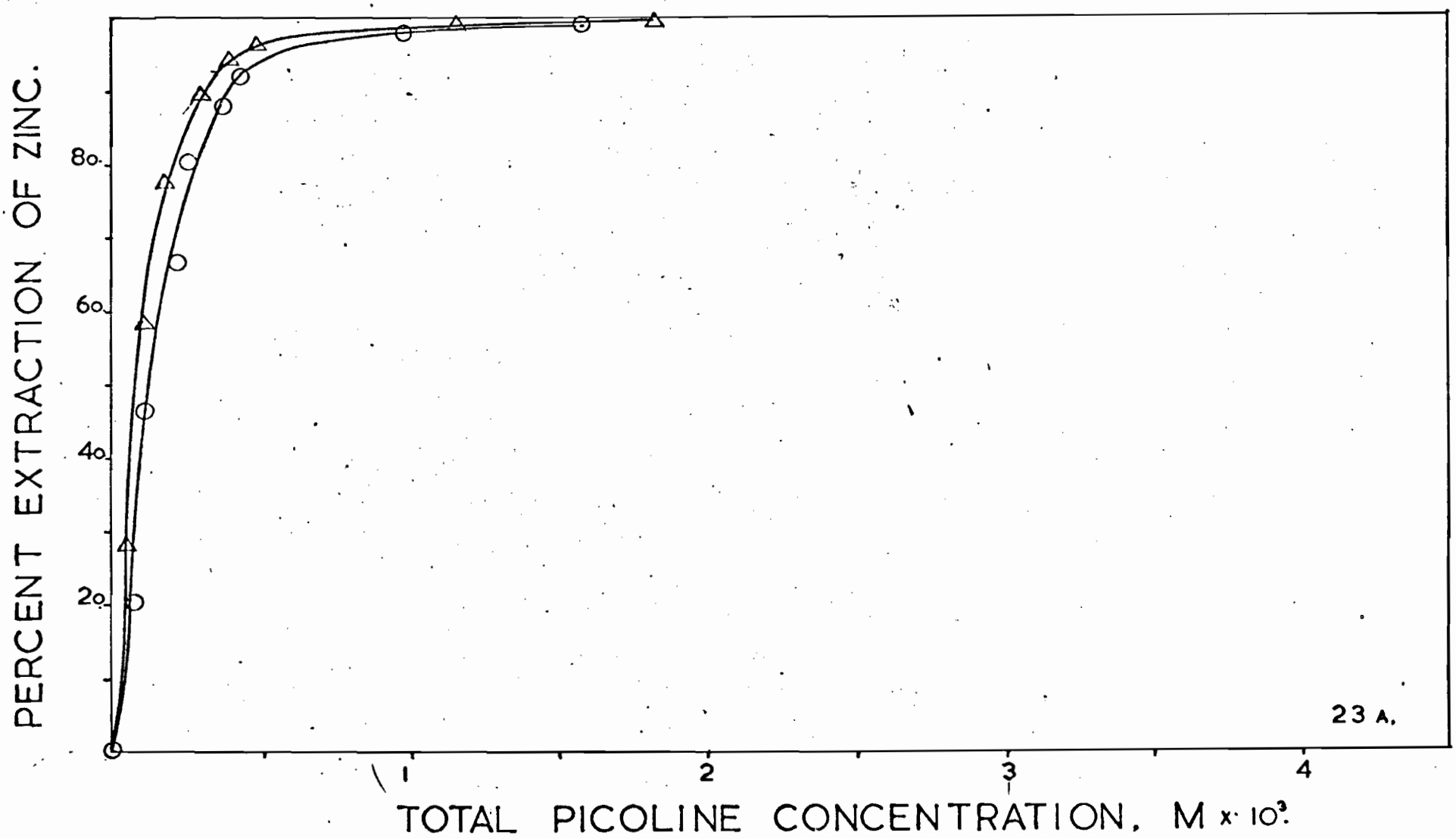
*** The molar ratio of thiocyanate to zinc in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known zinc concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

FIGURES 23A AND 23B

Extraction of zinc 3-picoline and 4-picoline thiocyanates into chloroform, as a function of the total equilibrium concentration of the picoline in the aqueous phase; the percent extraction (23A) and the distribution ratio (23B) in the presence of 0.001-M picolinium chloride.

⊙ = 3-picoline extractions.

△ = 4-picoline extractions.


PERCENT EXTRACTION OF ZINC.
80
60
40
20
1
2
3
4
TOTAL PICOLINE CONCENTRATION, M x 10³.
23 A.

23 B.

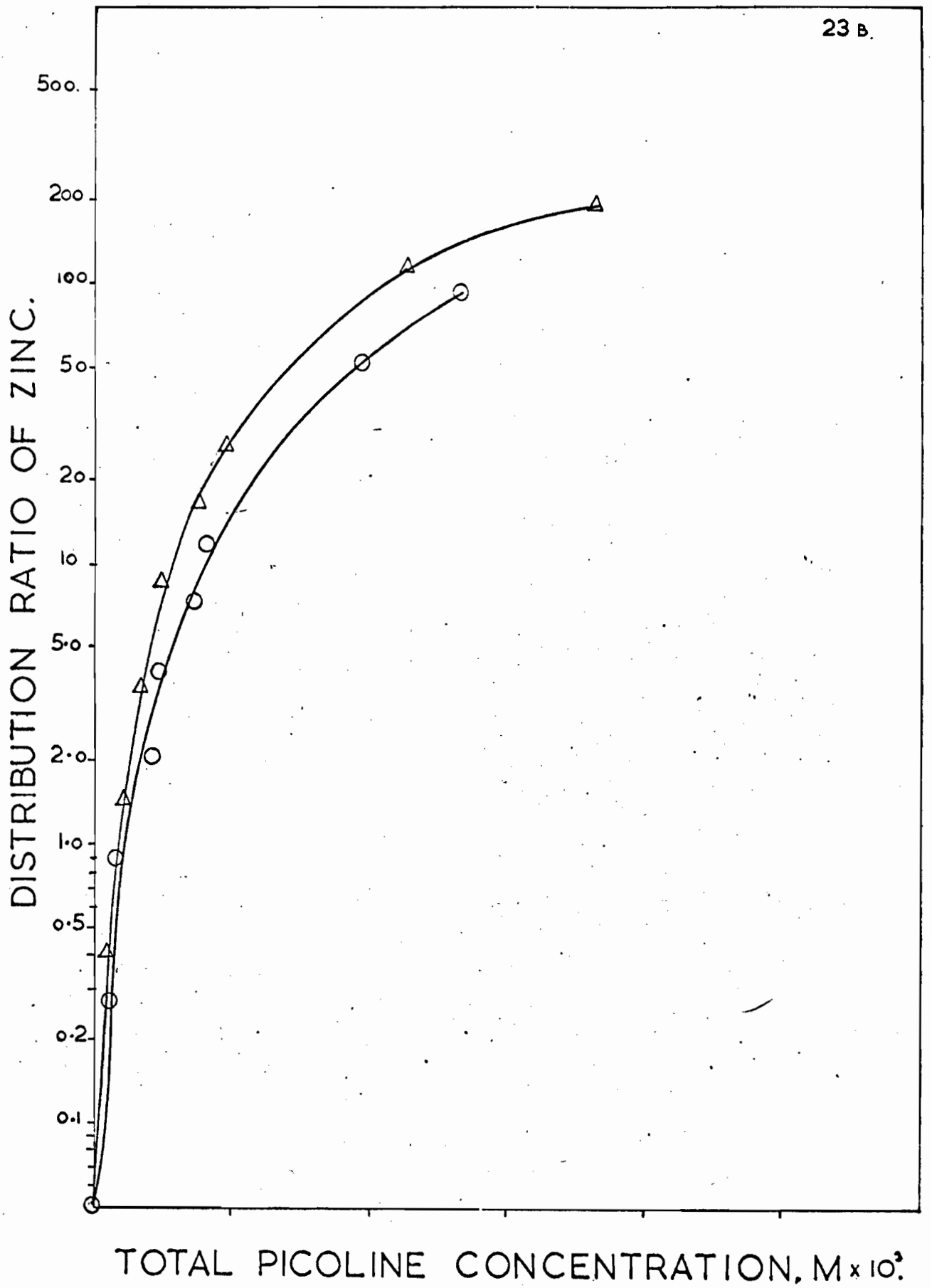

500.
200
100
50
20
10
5·0
2·0
1·0
0·5
0·2
0·1
DISTRIBUTION RATIO OF ZINC.
TOTAL PICOLINE CONCENTRATION, M x 10³.

TABLE LVII A

Effect of the 3-picoline concentration, in the presence of 3-picolinium chloride, on the distribution of cadmium between chloroform and aqueous thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cadmium				3-Picoline		Thiocyanate*	3-Picolinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O	Taken, mg (in H_2O)		
1	12.86	-	0	-	0	-	1391	0.001	-
2	"	12.65	0.09	12.74	151.9	2.44	1391	"	5.24
3	"	11.50	1.29	12.79	284.7	5.03	1395	"	5.50
4	"	9.00	3.79	12.79	379.8	6.43	1391	"	5.67
5	"	6.59	6.24	12.83	474.7	8.16	1391	"	5.76
6	"	4.30	8.56	12.86	569.5	9.66	1395	"	5.80
7	"	2.27	10.69	12.96	721.6	11.8	1391	"	5.90
8	"	0.662	12.25	12.91	854.0	14.8	1395	"	6.03
9	"	0.280	-	-	1152.	18.7	1391	"	6.17
10	"	0.090	-	-	1728.	29.5	1391	"	6.36

* Neither phase was analysed for thiocyanate.

TABLE LVII B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for cadmium 3-picoline thiocyanate extractions*

Ext. No.	Cadium				3-Picoline		Thiocyanate***	
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O	$CHCl_3$
1	1.25**	0	0	0	-	-	262.7	0
2	1.24	0.00910	0.00733	0.703	0.288	18.2	263.0	0.018
3	1.13	0.130	0.115	10.0	0.594	34.1	263.8	0.260
4	0.882	0.382	0.433	29.6	0.760	45.5	263.0	0.774
5	0.647	0.628	0.971	48.7	0.966	56.7	263.0	1.26
6	0.423	0.861	2.04	66.7	1.15	68.0	263.7	1.72
7	0.223	1.07	4.80	82.5	1.40	86.1	262.7	2.14
8	0.0652	1.23	18.9	94.9	1.76	102	263.8	2.46
9	0.0277	1.26**	45.5	97.9	2.23	137	263.8	2.52
10	0.00895	1.27**	142	99.3	3.55	204	265.3	2.54.

* Basic data are in Table LVII A.

** Calculated by difference.

*** The molar ratio of thiocyanate to cadmium in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known cadmium concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

TABLE LVIII A

Effect of the 4-picoline concentration, in the presence of 4-picolinium chloride, on the distribution of cadmium between chloroform and aqueous thiocyanate solutions

Initial volume of each phase : 90 ml.
Final phase volumes : See Table IV.
Mechanical shaking time : 10 minutes.
Extraction temperature : 25.0°C.

Ext. No.	Cadmium				4-Picoline		Thiocyanate*	4-Picolinium chloride molarity	Equil. pH of H_2O phase
	Taken, mg (in H_2O)	Found, mg H_2O	Found, mg $CHCl_3$	Found, mg Total	Taken, mg (in H_2O)	Found, mg H_2O	Taken, mg (in H_2O)		
1	12.86	-	0	-	0	-	1391	0.001	-
2	"	12.73	0.090	12.82	94.9	1.82	1391	"	5.48
3	"	11.11	1.31	12.42	189.8	3.68	1391	"	5.76
4	"	7.79	5.02	12.81	284.8	5.48	1395	"	5.91
5	"	4.33	8.53	12.86	379.6	6.94	1391	"	6.06
6	"	2.09	10.56	12.65	474.5	8.92	1391	"	6.13
7	"	1.13	11.52	12.65	569.7	10.50	1395	"	6.20
8	"	0.350	12.40	12.75	721.2	13.46	1391	"	6.33
9	"	0.138	12.54	12.68	854.0	16.17	1395	"	6.34
10	"	0.020	-	-	1322	25.20	1391	"	6.58

* Neither phase was analysed for thiocyanate.

TABLE LVIII B

Distribution ratio (D), percent extraction (E) and molar concentrations (M) for cadmium 4-picoline thiocyanate extractions*

Ext. No.	Cadmium				4-picoline		Thiocyanate***	
	Found, M x 10^3 H_2O	$CHCl_3$	D	E	Found, M x 10^3 H_2O	$CHCl_3$**	Found, M x 10^3 H_2O	$CHCl_3$
1	1.25**	0	0	0	-	-	262.7	0
2	1.24	0.0091	0.00734	0.704	0.215	11.4	263.0	0.0182
3	1.09	0.132	0.121	10.5	0.444	22.7	263.0	0.264
4	0.763	0.507	0.664	39.2	0.648	34.1	263.3	1.14
5	0.424	0.860	2.03	66.4	0.821	45.4	262.0	1.72
6	0.205	1.06	5.17	83.4	1.06	56.6	262.2	2.12
7	0.111	1.16	10.5	91.1	1.25	68.0	263.0	2.32
8	0.0340	1.25	36.8	97.3	1.60	85.8	262.3	2.50
9	0.0136	1.26	92.7	98.9	1.97	101	263.7	2.52
10	0.002	1.28**	640	99.9	3.04	156	264.0	2.56

* Basic data are in Table LVIII A.

** Calculated by difference.

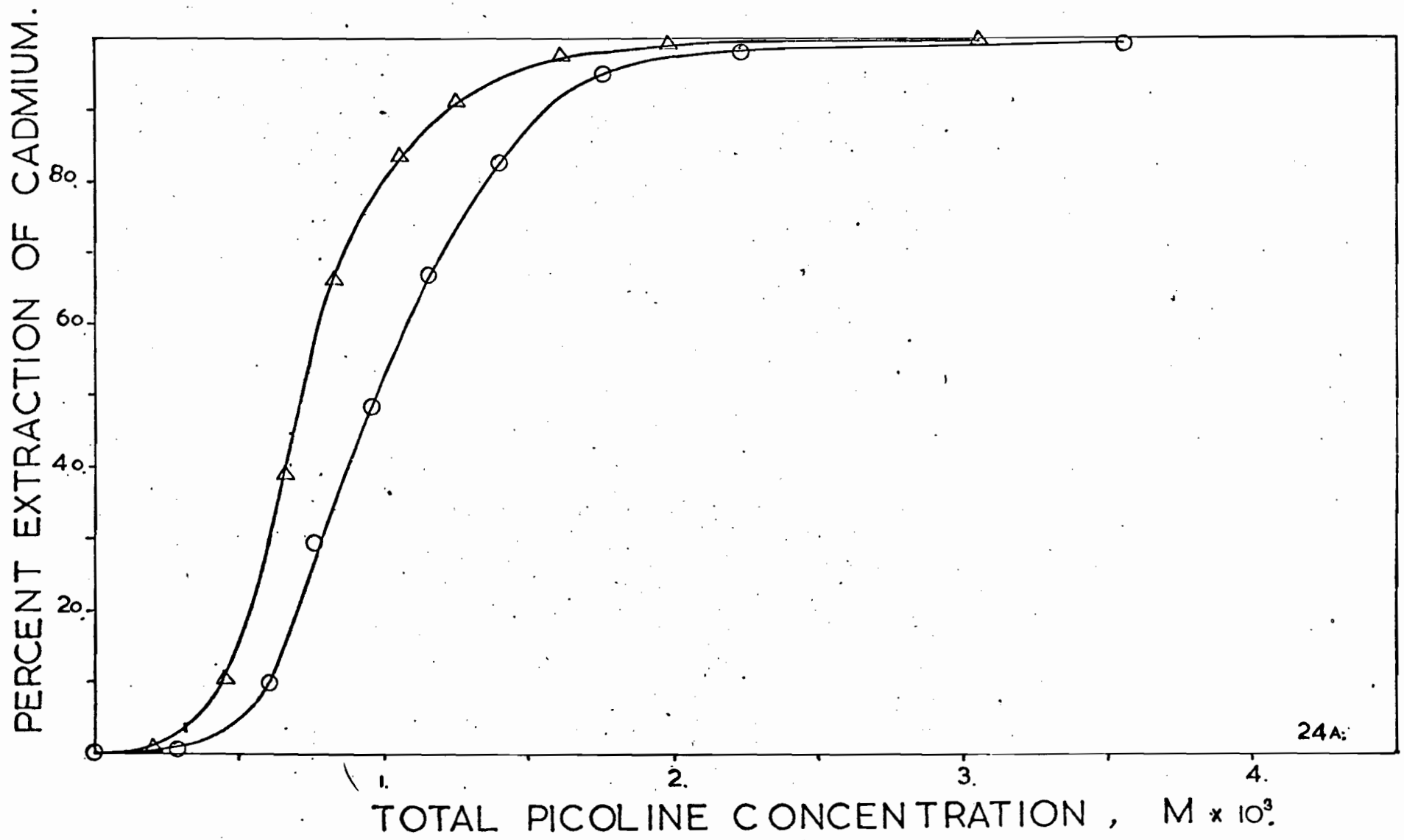
*** The molar ratio of thiocyanate to cadmium in the chloroform phase was assumed to be 2.00. The concentration of thiocyanate in the chloroform phase was calculated from this ratio and the known cadmium concentration of that phase. Then the concentration of thiocyanate in the aqueous phase was calculated by difference.

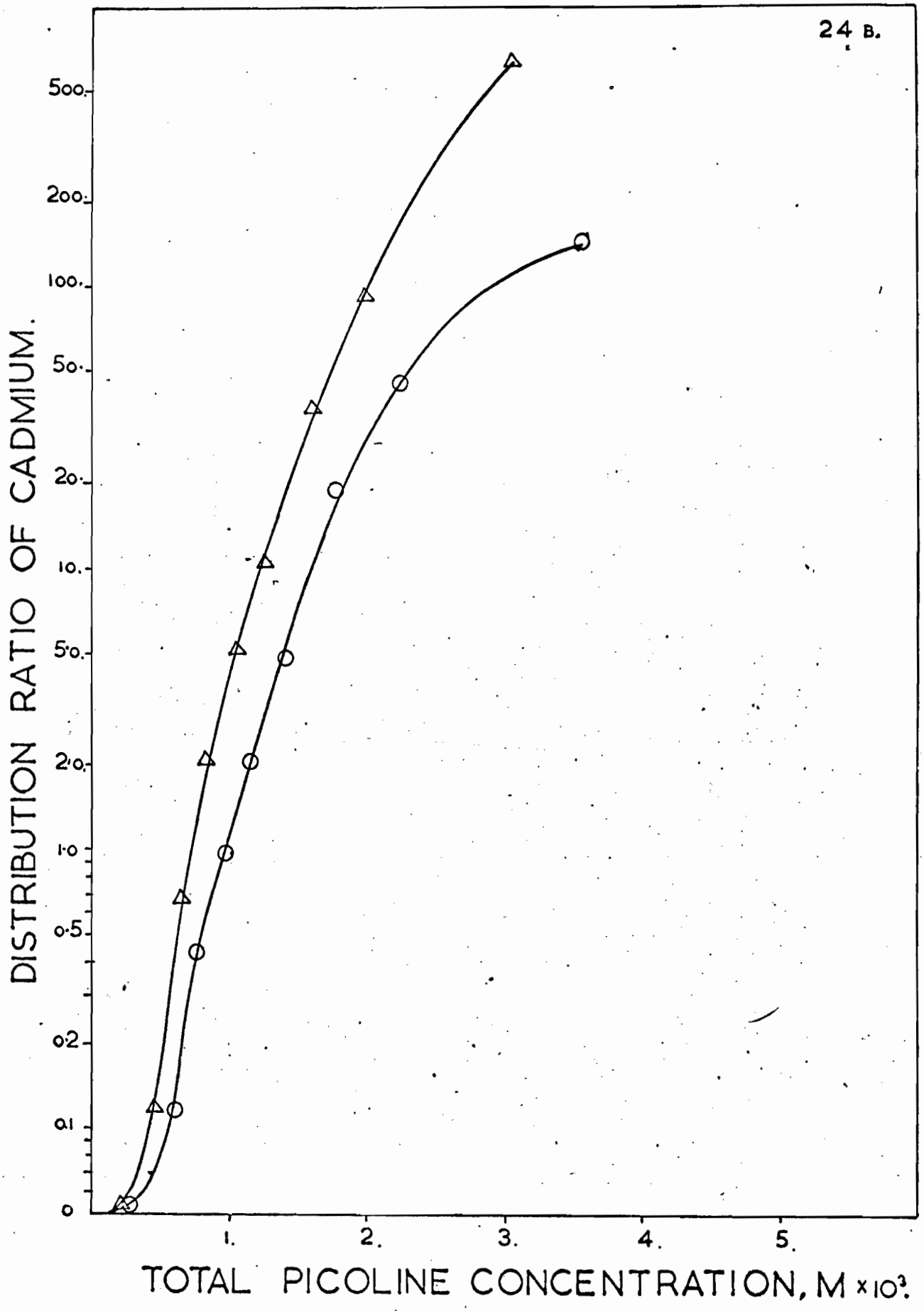
FIGURES 24A AND 24B

Extraction of cadmium 3-picoline and 4-picoline thiocyanates into chloroform, as a function of the total equilibrium concentration of the picoline in the aqueous phase; the percent extraction (24A) and the distribution ratio (24B) in the presence of a 0.001-M picolinium chloride.

⊙ = 3-picoline extractions.

△ = 4-picoline extractions.


PERCENT EXTRACTION OF CADMIUM.
80.
60.
40.
20.
1.
2.
3.
4.
TOTAL PICOLINE CONCENTRATION , M x 10³.
24A.


24 B.
DISTRIBUTION RATIO OF CADMIUM.
500.
200.
100.
50.
20.
10.
5·0.
2·0.
1·0
0·5
0·2
0·1
0
1.
2.
3.
4.
5.
TOTAL PICOLINE CONCENTRATION, M x 10³.

PART VI

TREATMENT OF THE ANALYTICAL DATA, AND PRELIMINARY DISCUSSION

1. The Apparent Partition Coefficients* of Free Pyridine and Free Picolines Between Chloroform and Aqueous 0.3-M Potassium Thiocyanate Solution in the Metal Pyridine and Picoline Thiocyanate Extraction Systems**

The measured distribution ratios of pyridine and the picolines between chloroform and aqueous 0.3-M potassium thiocyanate solution in the absence of metal are given in Table LIX. These values will henceforth be assumed to be the partition coefficients.

In order to compare these partition coefficients with those obtained when a metal pyridine or picoline thiocyanate complex was present in the extraction system, it was first necessary to define the apparent partition coefficient, p*.

$$p^* = \frac{[P]_{T,o} - 2[MP_2T_2]_o - 4[MP_4T_2]_o}{[P]_{T,A}} \qquad (23)$$

where $[P]_{T,o}$ and $[P]_{T,A}$ are the total concentrations of pyridine (or picoline) in the organic and aqueous phases, respectively; and $[MP_2T_2]_o$ and $[MP_4T_2]_o$ are the concentrations, in the organic phase, of metal dipyridine (or dipicoline) thiocyanate and metal tetrapyridine (or tetrapicoline) thiocyanate, respectively. The data in Tables XXIX to LVIII were used to evaluate p*, by the method described below.

Of the four parameters which define p* in equation (23), only the values of $[P]_{T,o}$ and $[P]_{T,A}$ were known by experiment. It was therefore necessary to make two assumptions so that working values of p* could be calculated:

---

* These partition coefficients will in all cases refer to a ratio of molar concentrations, with the concentration in the organic phase being in the numerator.

** Throughout the present Section, molarities will be understood when concentrations are stated or discussed. Total concentrations will always mean stoichiometric concentrations.

TABLE LIX

Mean values of the partition coefficient, p, of pyridine and the picolines between chloroform and aqueous 0.3-M potassium thiocyanate solution at 25.0°C

Partitioned reagent	Pyridinium or picolinium chloride added, M	p	N	s_x
Pyridine	0	14.1	16	0.3
2-Picoline	0	41.2	2	-
3-Picoline	0	54.7	10	1.0
4-Picoline	0	47.2	10	0.8
Pyridine	0.001	14.1	15	0.3
2-Picoline	0.001	43.2	2	-
3-Picoline	0.001	57.2	10	0.8
4-Picoline	0.001	49.6	10	0.6

NOTES: (1) The values in the Table are taken from Tables XXXVI, XXXVIII and XXXIX.

(2) N is the number of replicate experiments and s_x is the standard deviation based on N-1 degrees of freedom.

(3) The partition coefficient of pyridine between benzene and water at 25°C has been reported (67) to be 2.93.

(4) The concentration of pyridine (or picoline) in the equilibrated aqueous phase was about 8×10^{-4}M.

(1) For all* those extraction systems containing cobalt, nickel or cadmium, the metal in the organic phase was assumed to be present as the tetrapyridine or tetrapicoline thiocyanate. Then, since the total concentration of metal in the organic phase, $[M]_{T,o}$, was known, the apparent partition coefficient, p*, was computed, for these extraction systems, from the relationship

$$p^* = \frac{[P]_{T,o} - 4[M]_{T,o}}{[P]_{T,A}} \qquad (24)$$

(2) For all those extraction systems containing zinc, the metal in the organic phase was assumed to be present as the dipyridine or dipicoline thiocyanate. Then, since the total concentration of metal in the organic phase, $[M]_{T,o}$, was known, the apparent partition coefficient, p*, was computed, for these extractions systems, from the relationship

$$p^* = \frac{[P]_{T,o} - 2[M]_{T,o}}{[P]_{T,A}} \qquad (25)$$

These values of p* then were plotted against the total concentration of pyridine or picoline in the aqueous phase. The graphs are shown in Figs. 25 to 46. The data from which the graphs were drawn are in Appendix XVI.

Despite the inevitable scatter in the points, two distinct trends seemed evident in most of these graphs:

(i) Extrapolation to zero concentration of pyridine or picoline gave p**, the apparent partition coefficient at zero concentration of

---

* The cobalt 2-picoline thiocyanate system was not treated, for reasons discussed below.

FIGURES 25 to 46

The apparent partition coefficients, p^*, of pyridine and the picolines between chloroform and aqueous 0.3-M potassium thiocyanate solutions at 25.0°C in the metal pyridine and picoline thiocyanate extraction systems, versus the total concentration of pyridine (or picoline) in the aqueous phase, $[P]_{T,A}$.

NOTES: (1) The data for these graphs are in Appendix XVI.

(2) The solid lines represent the variation of another partition coefficient, p_t, with $[P]_{T,A}$; p_t is defined by equation (39); it is used later for the calculations given in Appendix XVI.

(3) All metal concentrations specified in the Figures are the values initially present in the aqueous phases before equilibration.

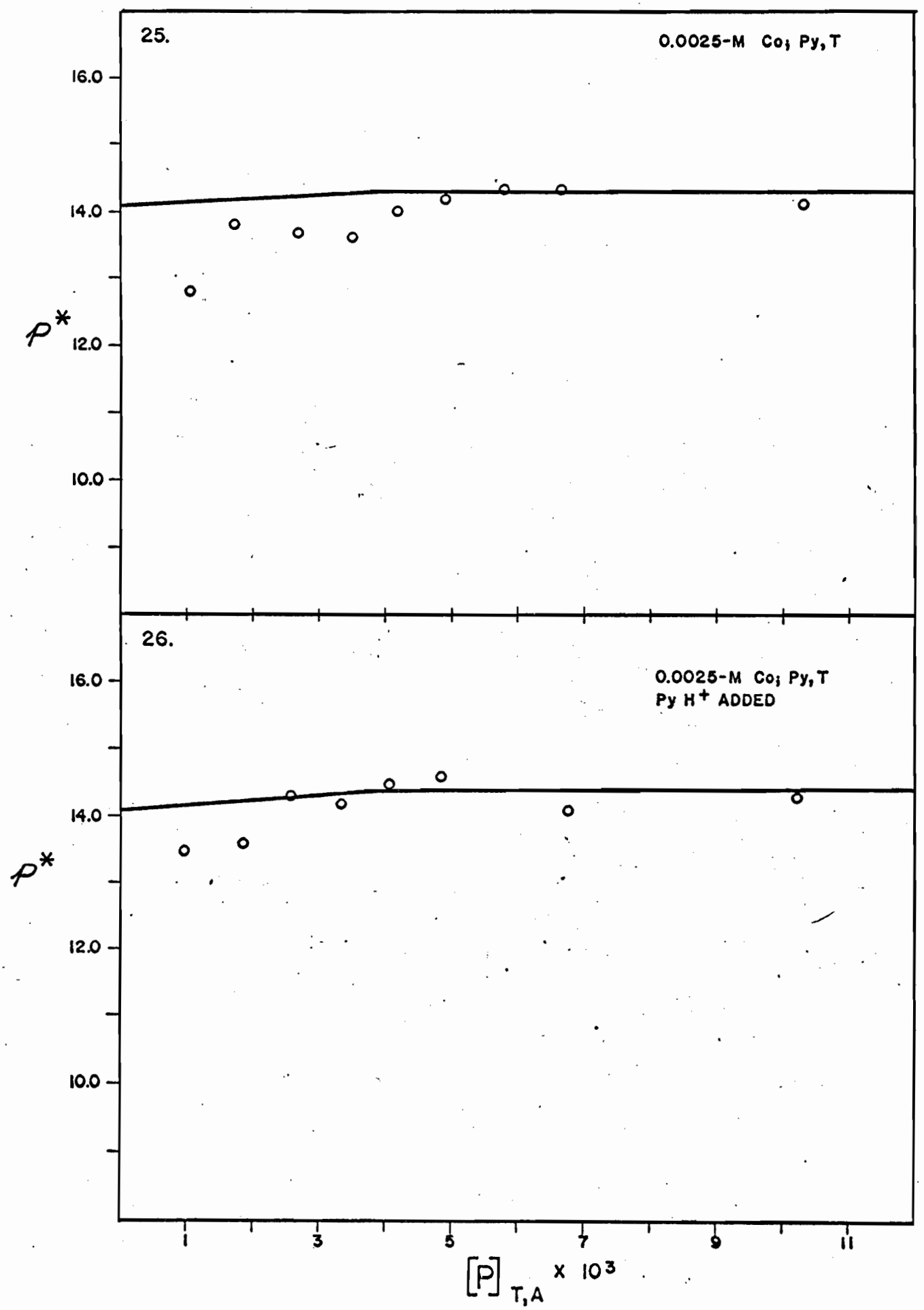
LEGEND: Py = pyridine

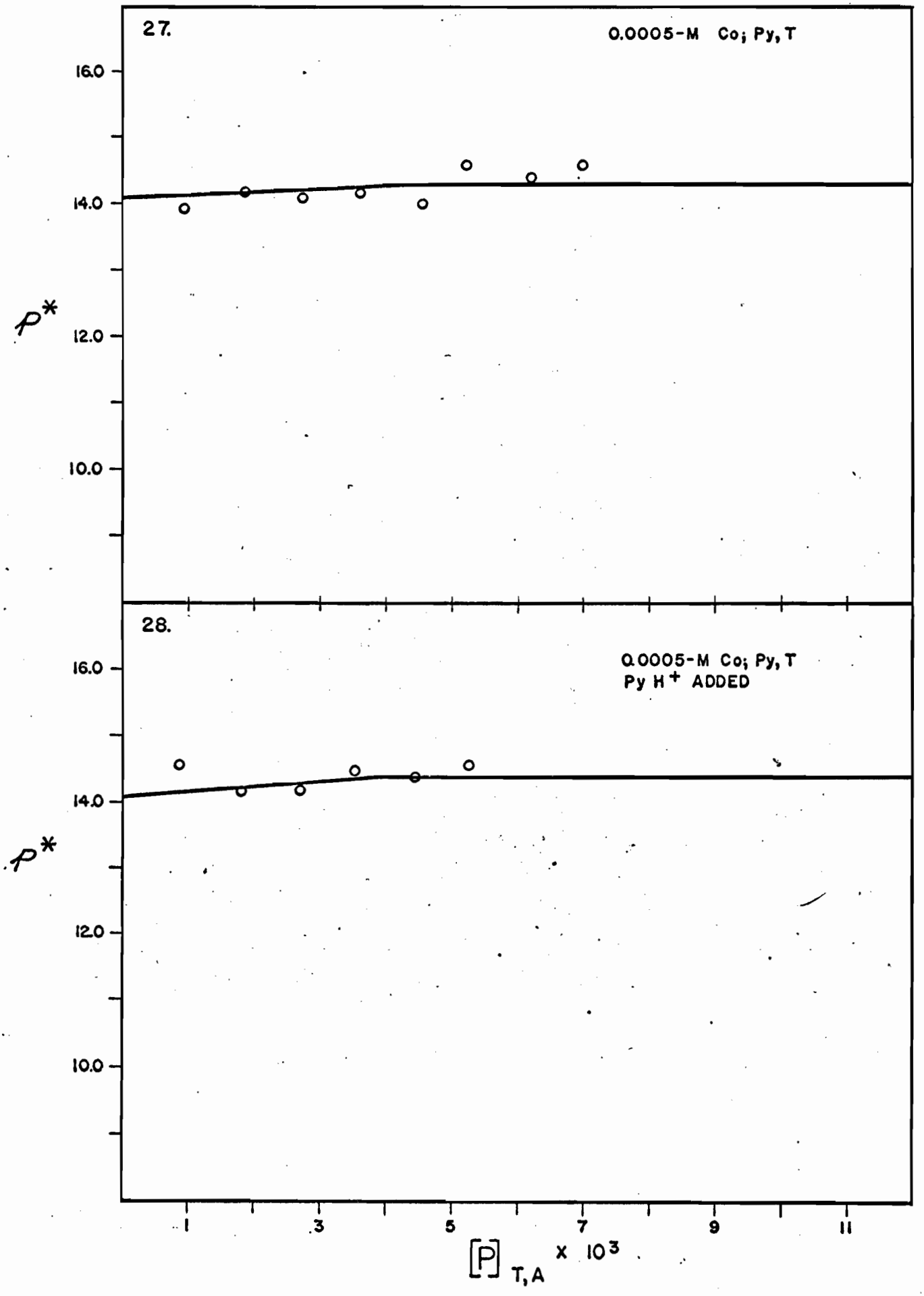
Pic = picoline

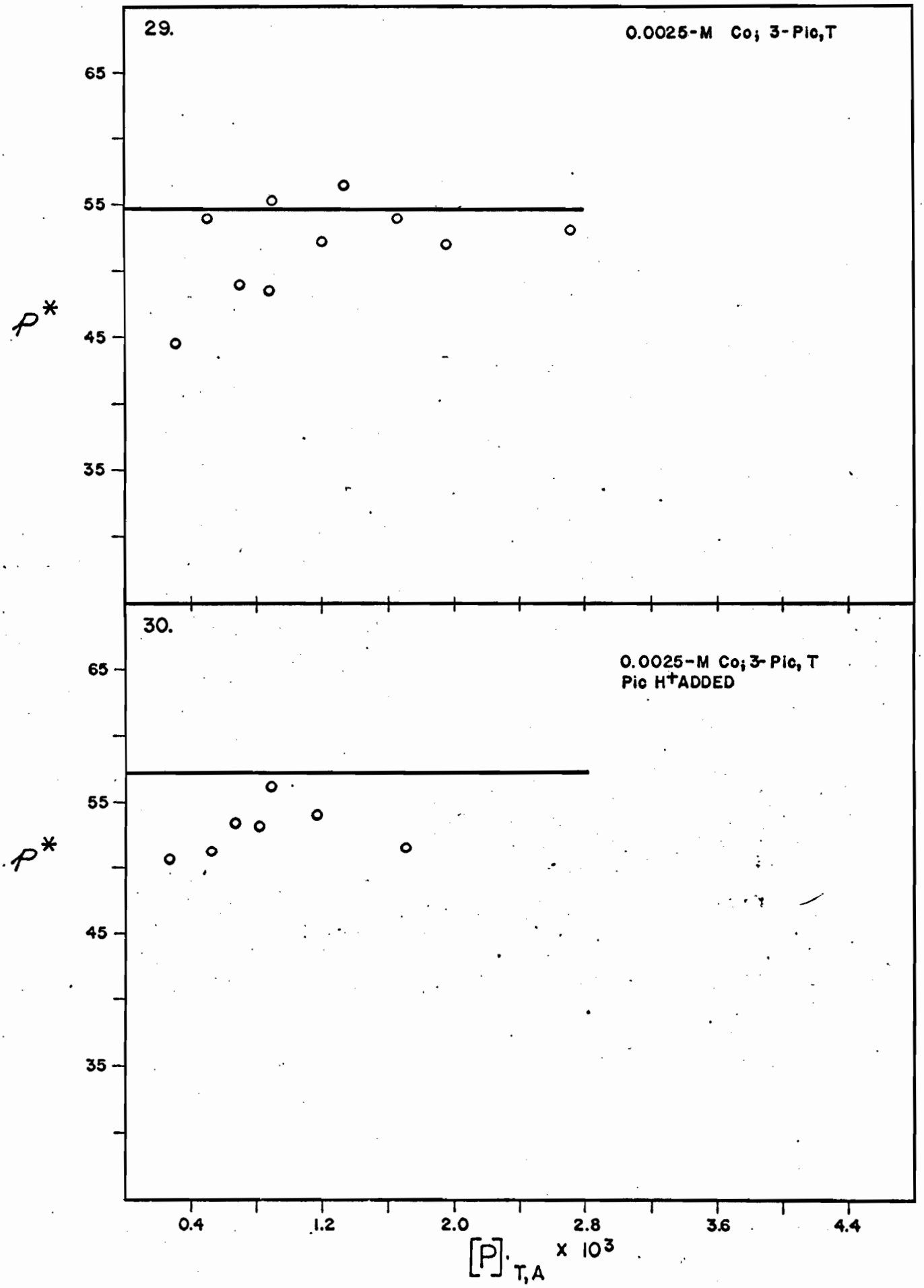
PyH^+ = pyridinium ion

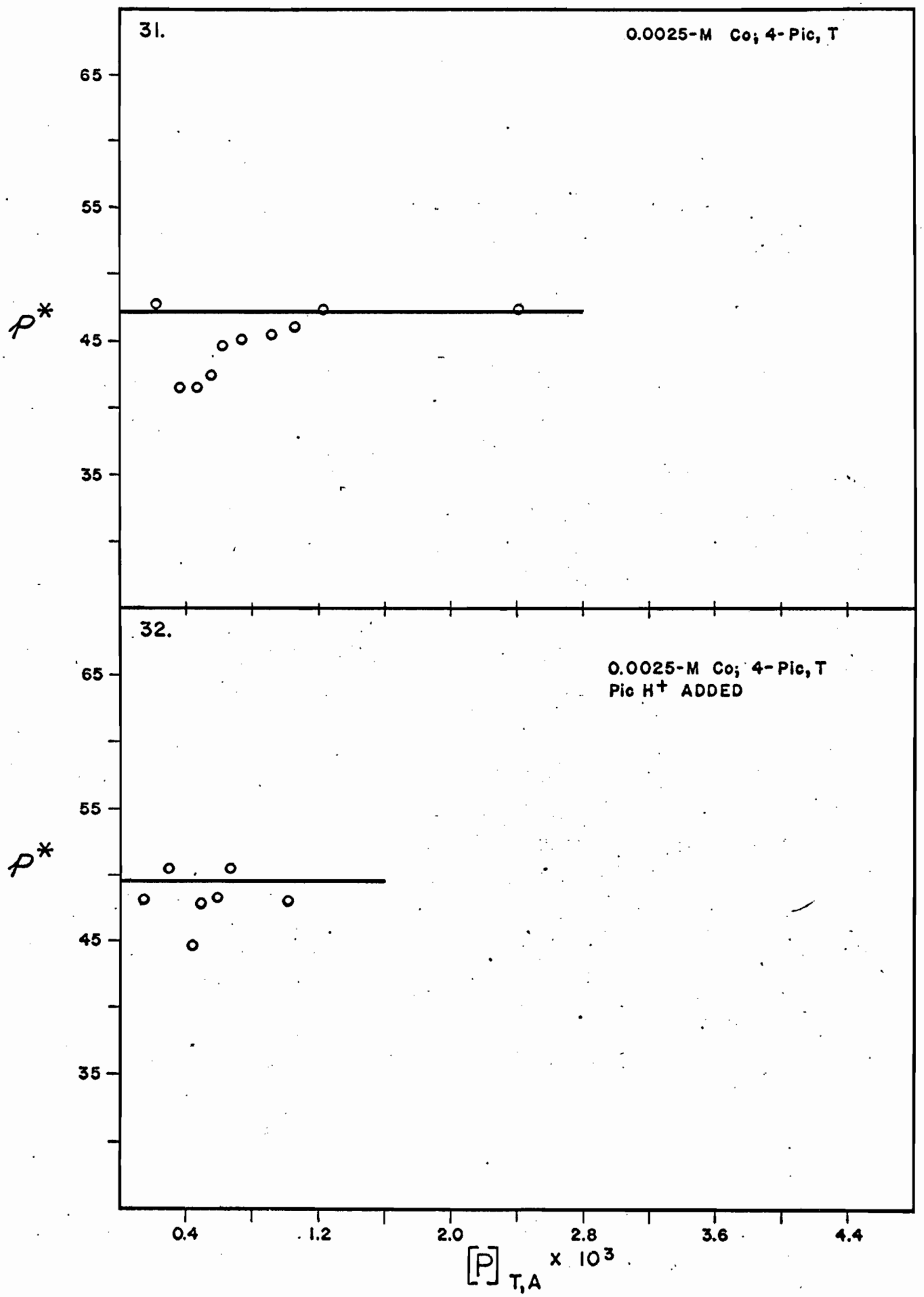
$PicH^+$ = picolinium ion

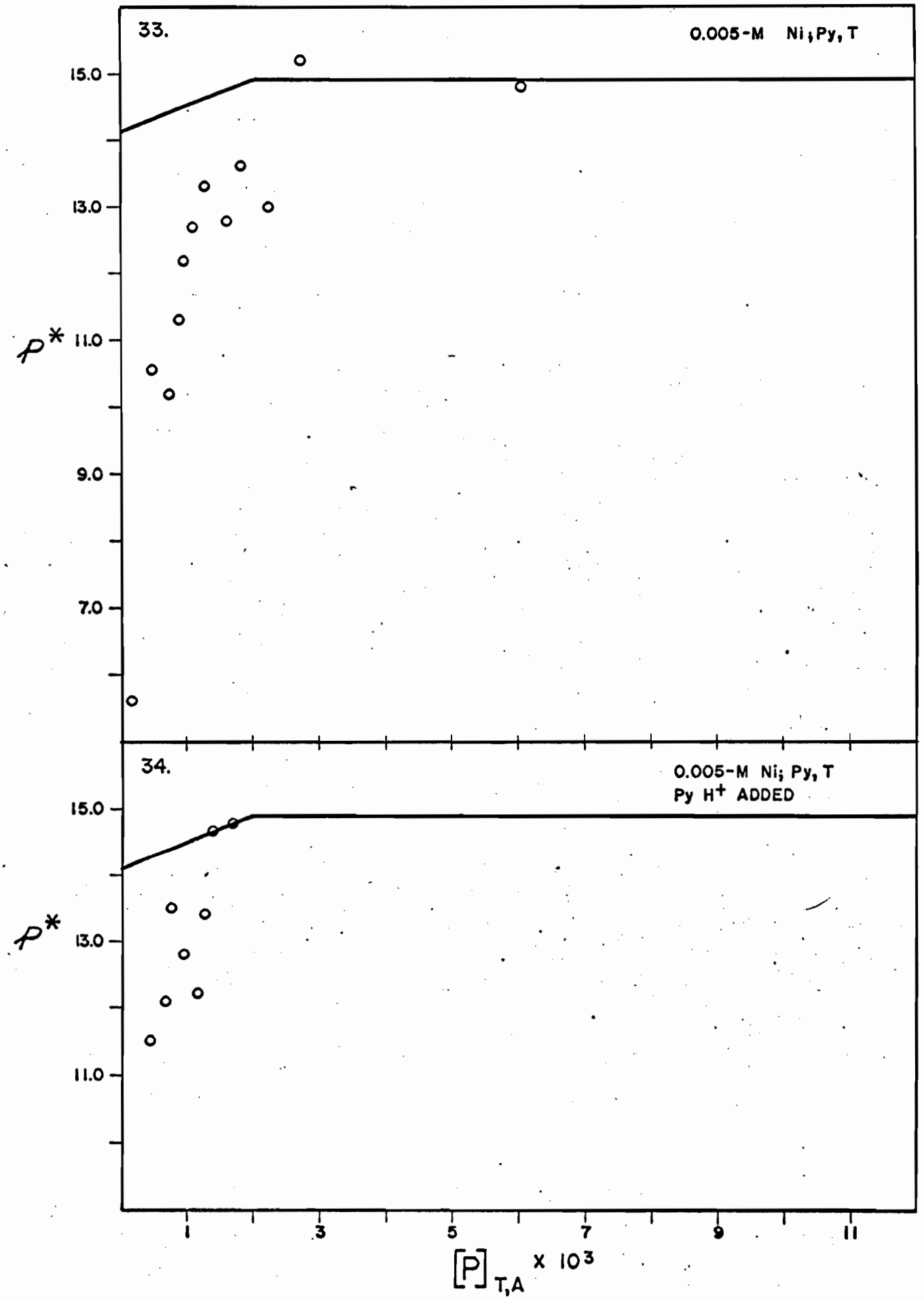
T = thiocyanate

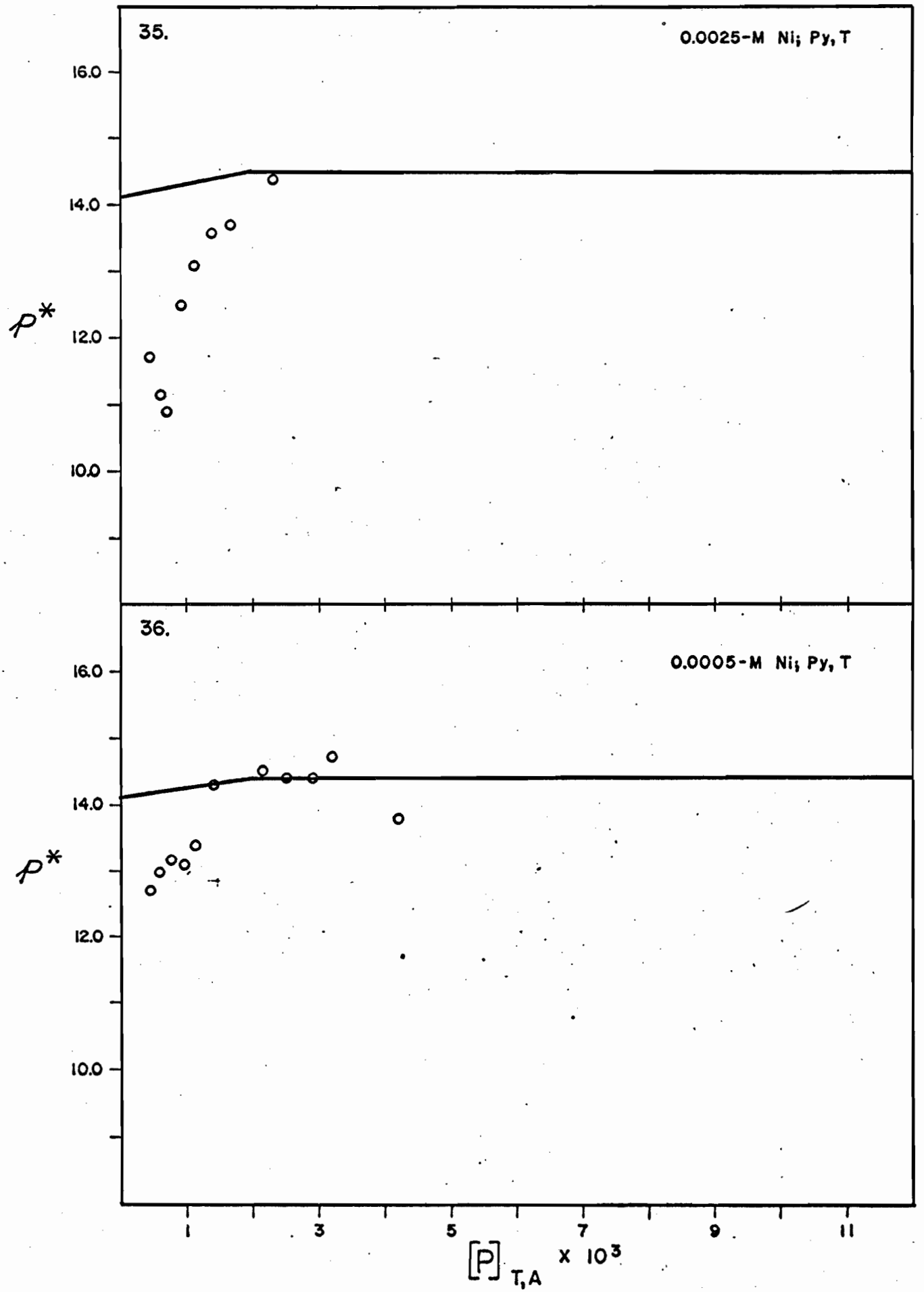

25.
0.0025-M Co; Py, T
16.0
14.0
12.0
10.0
p*
26.
0.0025-M Co; Py, T
Py H+ ADDED
16.0
14.0
12.0
10.0
p*
1
3
5
7
9
11
[P] T,A X 10³

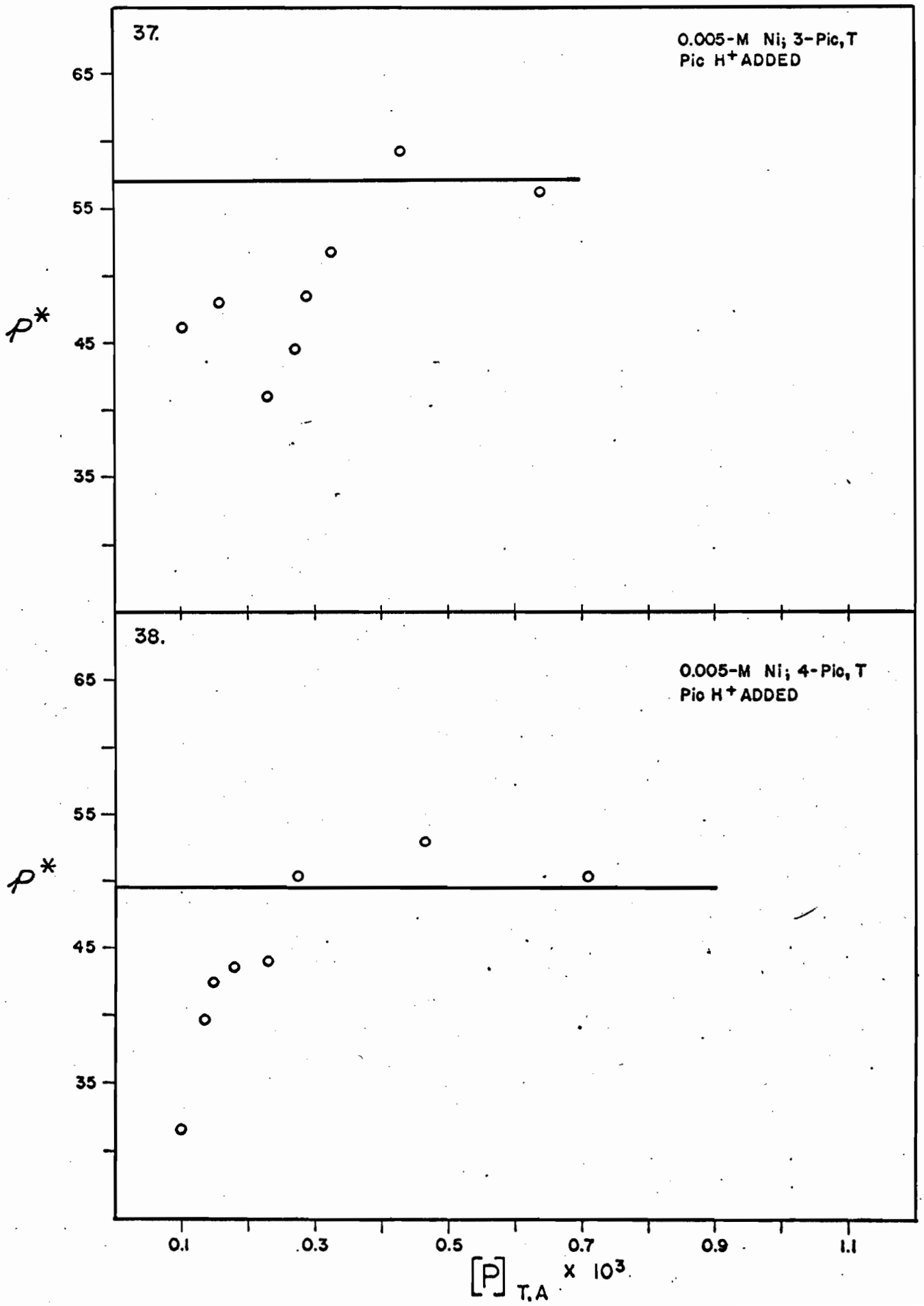

27.
0.0005-M Co; Py, T
16.0
14.0
12.0
10.0
p*
28.
0.0005-M Co; Py, T
Py H+ ADDED
16.0
14.0
12.0
10.0
p*
1
3
5
7
9
11
[P]T,A x 10^3

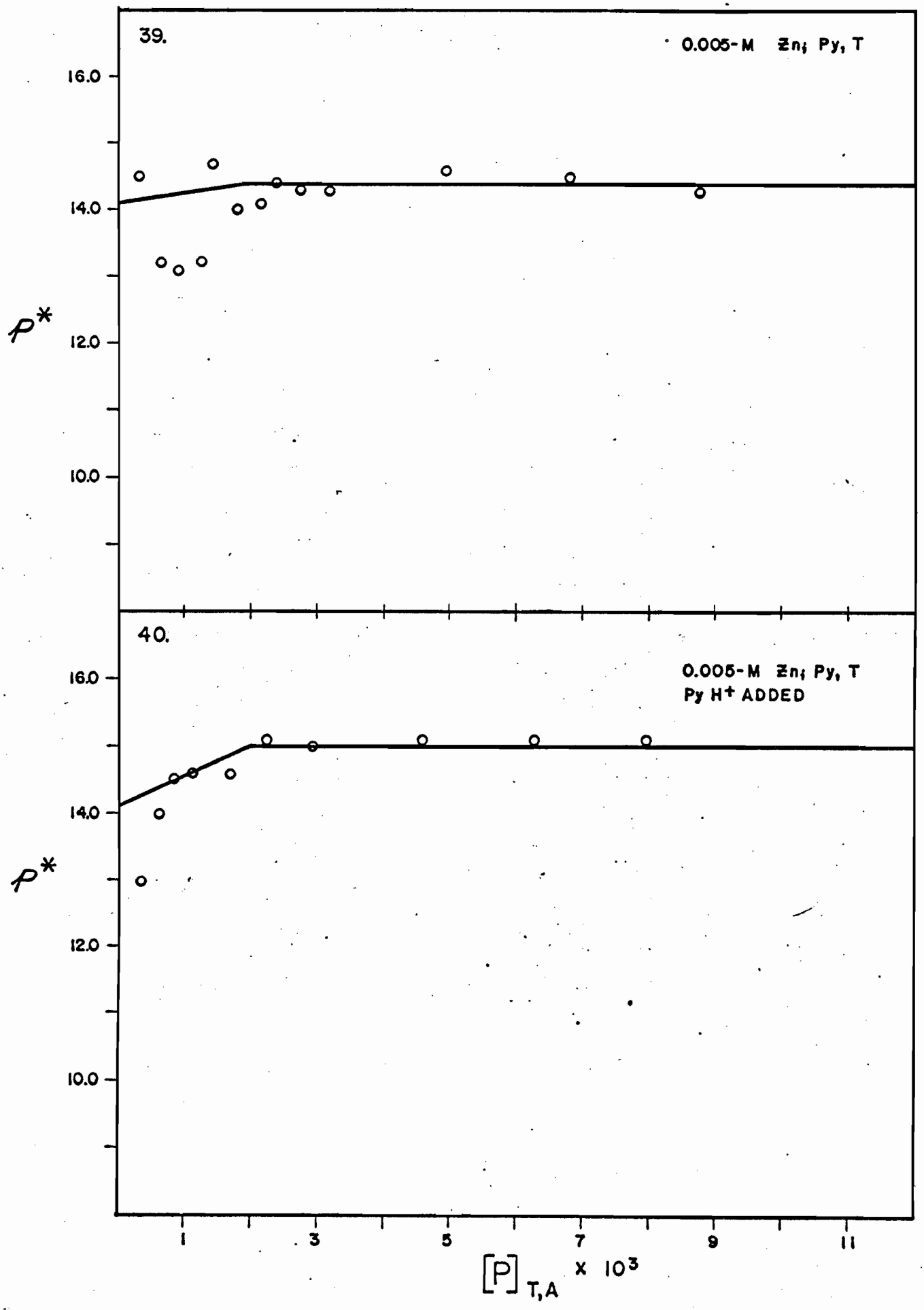

29.
0.0025-M Co; 3-Pic,T
65
55
45
35
p*
30.
0.0025-M Co; 3-Pic, T
Pic H+ADDED
65
55
45
35
p*
0.4
1.2
2.0
2.8
3.6
4.4
[P]T,A x 10^3

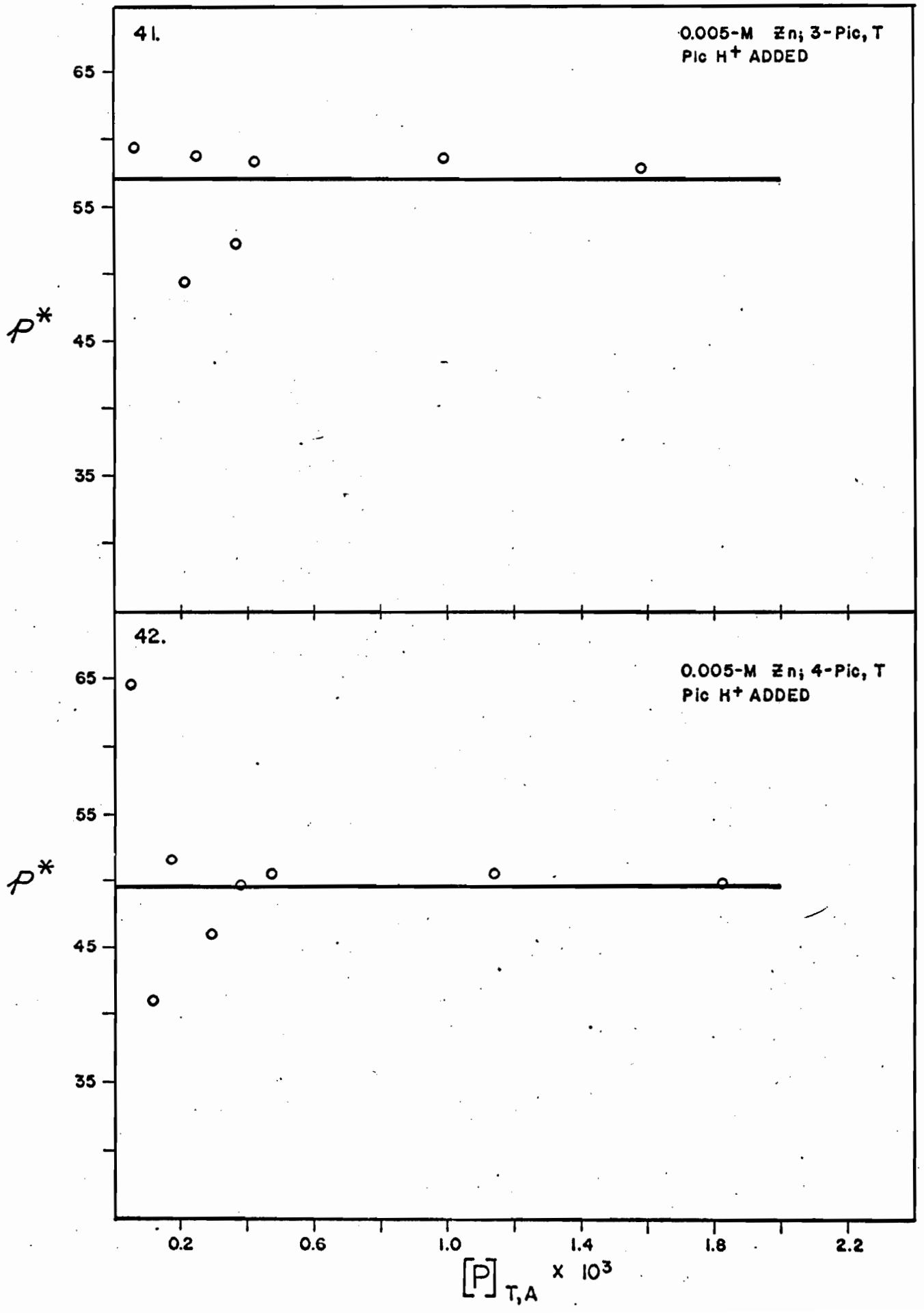

31.
0.0025-M Co; 4-Pic, T
65
55
45
35
ρ*
32.
0.0025-M Co; 4-Pic, T
Pic H+ ADDED
65
55
45
35
ρ*
0.4
1.2
2.0
2.8
3.6
4.4
[P]T,A x 10³

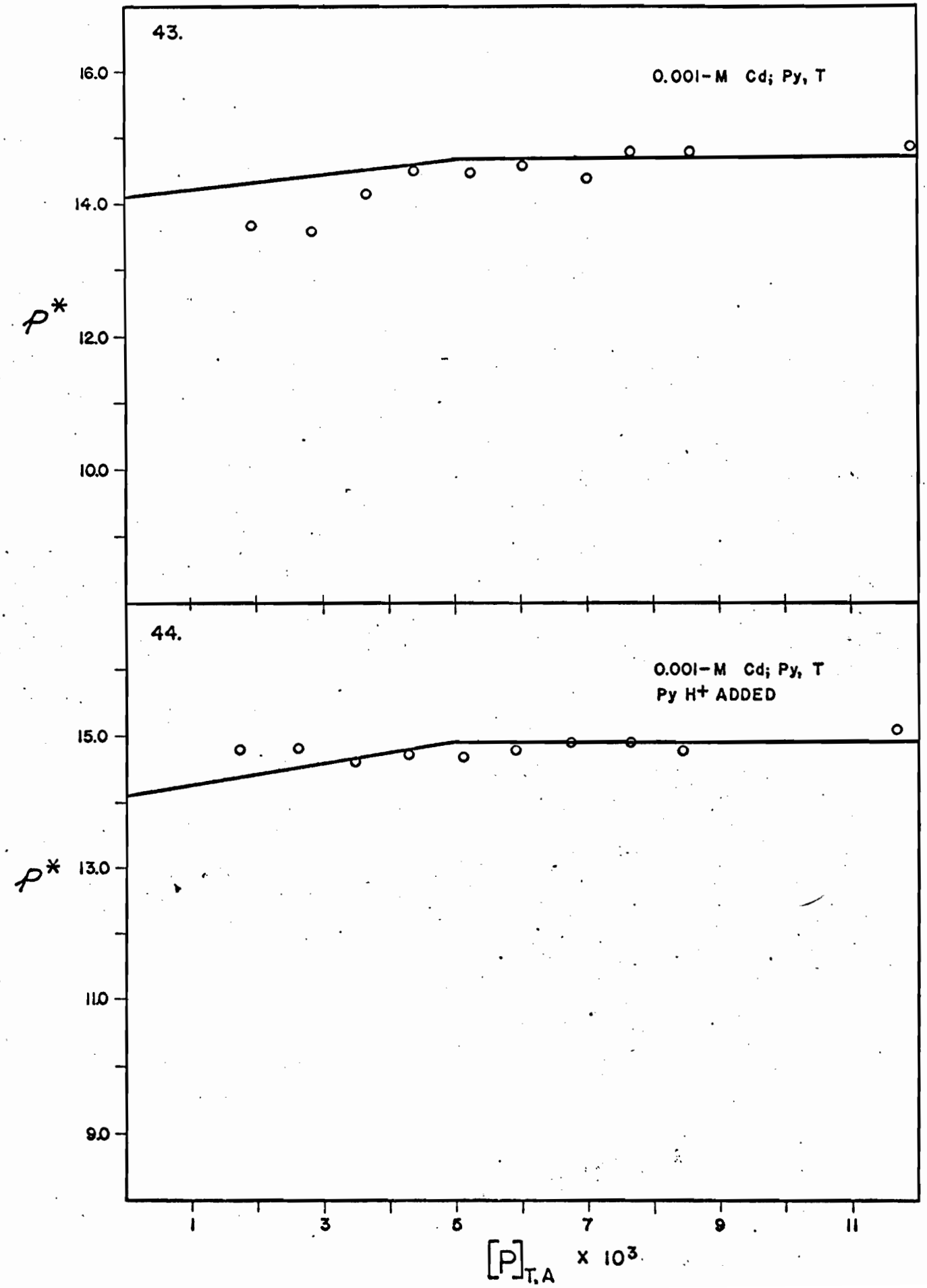

33.
0.005-M Ni;Py, T
15.0
13.0
11.0
9.0
7.0
p*
34.
0.005-M Ni; Py, T
Py H+ ADDED
15.0
13.0
11.0
p*
1
3
5
7
9
11
[P]T,A x 10^3

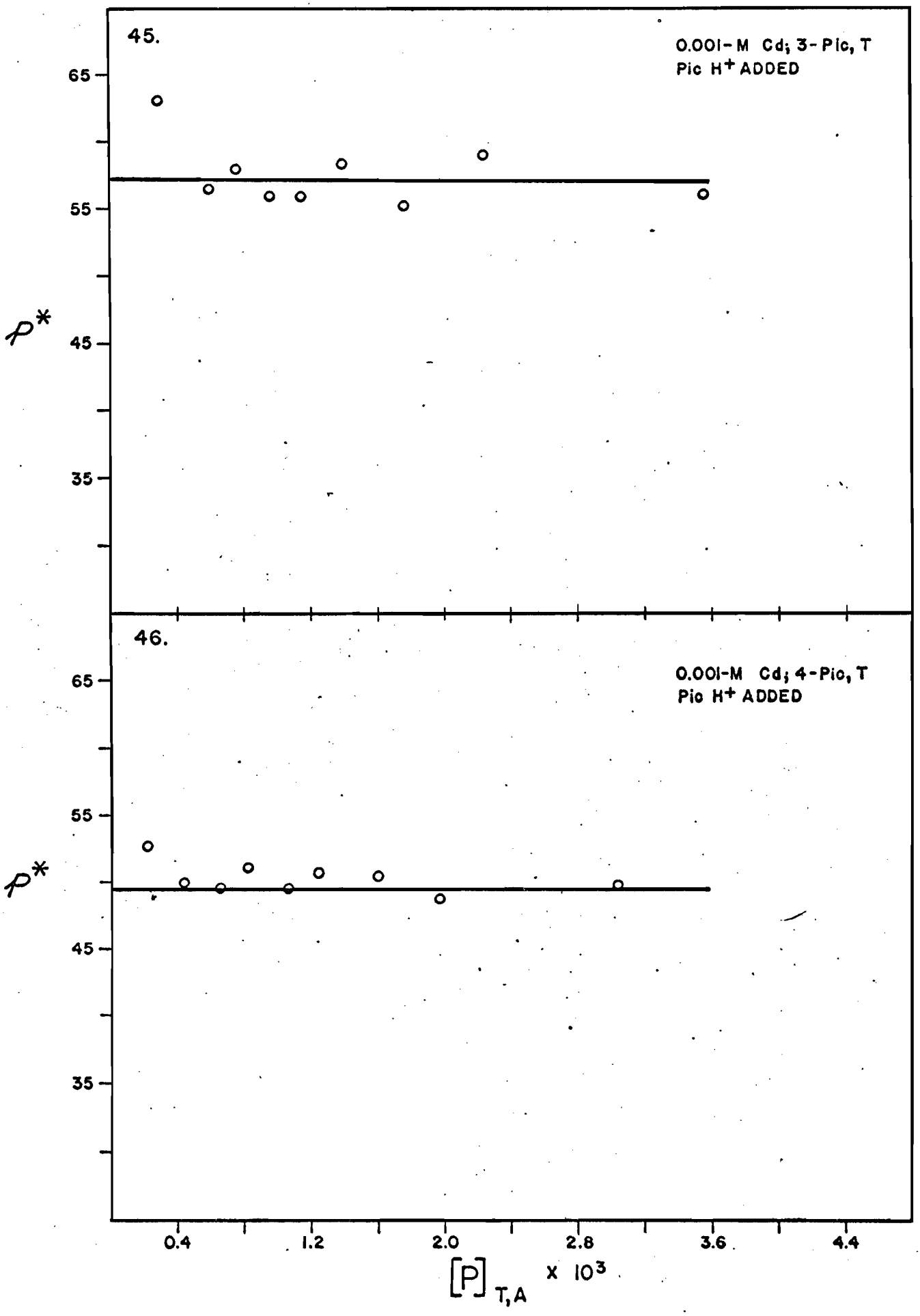

35.
0.0025-M Ni; Py, T
16.0
14.0
12.0
10.0
ρ*
36.
0.0005-M Ni; Py, T
16.0
14.0
12.0
10.0
ρ*
1
3
5
7
9
11
[P]T,A x 10³


37.
0.005-M Ni; 3-Pic, T
Pic H+ ADDED
65
55
45
35
p*
38.
0.005-M Ni; 4-Pic, T
Pic H+ ADDED
65
55
45
35
p*
0.1
0.3
0.5
0.7
0.9
1.1
[P]T.A x 10^3


39.
0.005-M Zn; Py, T
16.0
14.0
12.0
10.0
ρ*
40.
0.005-M Zn; Py, T
Py H+ ADDED
16.0
14.0
12.0
10.0
ρ*
1
3
5
7
9
11
[P]T,A x 10³


41.
0.005-M Zn; 3-Pic, T
Pic H+ ADDED
65
55
45
35
p*
42.
0.005-M Zn; 4-Pic, T
Pic H+ ADDED
65
55
45
35
p*
0.2
0.6
1.0
1.4
1.8
2.2
[P]T,A x 10^3


43.
0.001-M Cd; Py, T
16.0
14.0
12.0
10.0
ρ*
44.
0.001-M Cd; Py, T
Py H+ ADDED
15.0
13.0
11.0
9.0
ρ*
1
3
5
7
9
11
[P]T, A x 10³


45.
0.001-M Cd; 3-Pic, T
Pic H+ ADDED
65
55
45
35
p*
46.
0.001-M Cd; 4-Pic, T
Pic H+ ADDED
65
55
45
35
p*
0.4
1.2
2.0
2.8
3.6
4.4
[P]T,A x 10^3

pyridine or picoline in the presence of metal and thiocyanate in the aqueous phase. In many cases p** appeared to be less than p, the partition coefficient of pyridine or picoline in the absence of metal. Indeed, p* was apparently lower than p at the lower concentrations of pyridine or the picoline. It is to be noted that the partition coefficient of pyridine remained constant, in the absence of metal, as the concentration of pyridine in the extraction system approached zero*. These facts suggested the existence in the aqueous phase of pyridine (or picoline) complexes of the metal.

(ii) At higher concentrations of pyridine, the value of p* in all cases appeared to exceed that of p. This suggested additional loose bonding of pyridine in the organic phase. However, such loose bonding was not apparent in any of the metal picoline thiocyanate extraction systems. It is unclear why pyridine, and not the picolines, should exhibit this apparent tendency.

It was necessary to obtain the most reliable estimate of p**, the apparent partition coefficient of pyridine or picoline in the presence of metal and thiocyanate in the aqueous phase, at zero concentration of pyridine or picoline. In addition, it was necessary to obtain the most reliable estimate of another parameter, K', which is defined below in equation (36) where its use will be explained. To find the "best" values of K' and p**, a least-squares technique was devised. The technique makes use of equations which are derived in the following sub-section. The least-squares calculations are somewhat involved; they

---

* The data from which this conclusion was drawn are in Table XXXVII.

are in Appendix XVI. The "best" values of p** and K', together with their 95 percent confidence limits, are in Table LX.

It is seen in Table LX that for all the metal pyridine thiocyanate extraction systems which contained pyridinium chloride, the extrapolation to zero concentration of pyridine gave a value for p** that was somewhat larger than the corresponding value in the absence of pyridinium chloride. Only for the cobalt 3-picoline and 4-picoline thiocyanate systems were extractions carried out both in the presence and absence of added picolinium chloride; again the value of p** was greater when picolinium chloride was present. However, as noted in Part V-4-1, the effect of pyridinium or picolinium chloride was to reduce slightly the concentration of total pyridine (or picoline) in the aqueous phase and not to change the distribution ratio of the metal. The reason for this effect is not understood.

It is also seen in Table LX that as the initial concentration of metal in a given solvent-extraction system was decreased, the value of p** approached the known value, p, of the pyridine or picoline partition coefficient. This fact points clearly to the existence in the aqueous phase of pyridine (or picoline) complexes of the metal.

The decrease in the observed partition coefficient of the free ligand in the presence of metal can be explained by supposing* that some of the pyridine or picoline in the aqueous phase was present in one or more previously unreported mixed complexes of the general formula $MP_mT_n^{(2-n)}$.

* On the basis of this supposition, it is readily shown that the value of p** must be lower than the value of p which is defined by

$$p = \frac{[P]_o}{[P]} \qquad (26)$$

(footnote continued)

footnote continued

where $[P]_o$ and $[P]$ are the concentrations of free pyridine (or picoline) in the organic and aqueous phases, respectively.

Since

$$[P]_{T,A} = [P] + [P]_b \qquad (27)$$

where $[P]_b$ is the concentration of bound pyridine (or picoline) in the aqueous phase, then by using the relationships

$$[P]_b = \sum_{m=1} \sum_{n=1} m[MP_mT_n] + \sum_{r=1} r[MP_r] \qquad (28)$$

and

$$[MP_mT_n] = K_{m,n}[M][T]^n[P]^m \qquad (29)$$

and

$$[MP_r] = K_{r,o}[M][P]^r \qquad (30)$$

equation (23) becomes

$$p^* = \frac{[P]_{T,o} - 2[MP_2T_2]_o - 4[MP_4T_2]_o}{[P]\left[1 + \sum_{m=1} \sum_{n=1} m[M][T]^n[P]^{m-1} K_{m,n} + \sum_{r=1} r[M][P]^{r-1} K_{r,o} + \ldots\right]} \qquad (31)$$

For simplicity, the charges on the ions have been omitted. Here and elsewhere in the present Section they are understood. As the total concentration of pyridine or picoline in the solvent-extraction system approaches zero, then so must the total concentration of metal complexes in the organic phase (it was shown previously that the metal thiocyanates were not measurably extracted). Therefore,

$$\lim_{[P] \longrightarrow 0} p^* = p^{**} = \frac{p}{1 + \sum_{n=1} [MT_n] K_{1,n} + [M] K_{1,o}} \qquad (32)$$

TABLE LX

Extrapolated value, p**, of the apparent partition coefficient of pyridine (α-picoline) between chloroform and aqueous 0.3-M potassium thiocyanate solution, and the value of K', for each metal pyridine and picoline thiocyanate extraction system at 25.0 °C

Extraction system	Least-squares values		Upper and lower 95 percent confidence limits		Value of K' used to calculate [P]
	p**	K'	p**	K'	
0.0025-M Co; Py , T	13.3	23.3	13.44 , 13.16	18.4 , 28.2	23.3
0.0025-M Co; Py , T[a]	13.7	11.3	13.90 , 13.50	5.6 , 17.2	11.3
0.0005-M Co; Py , T	13.96	19.4	14.14 , 13.78	< 0 , 44.8	23.3
0.0005-M Co; Py , T[a]	14.15	< 0	14.36 , 13.94	< 0 , 21.7	11.3
0.0025-M Co; 2-Pic , T	-	-	-	-	-
0.0025-M Co; 3-Pic , T	48.2	52.4	49.7 , 46.7	39.3 , 66.8	52.4
0.0025-M Co; 3-Pic , T[a]	50,5	51.6	52.3 , 48.7	36.5 , 68.0	51.6
0.0025-M Co; 4-Pic , T	42.0	48.1	43.1 , 40.9	36.9 , 59.7	48.1
0.0025-M Co; 4-Pic , T[a]	48.0	13.0	49.8 , 46.2	< 0 , 28.7	13.0
0.005-M Ni; Py , T	8.5	129.	9.10 , 7.90	107. ,153.	129.
0.005-M Ni; Py , T[a]	11.4	46.3	11.95 , 10.85	35.2 , 58.7	46.3
0.0025-M Ni; Py , T	10.9	115.	11.22 , 10.58	101. ,130.	129.
0.0005-M Ni; Py , T	12.3	286.	12.50 , 12.10	250. ,323.	129.
0.0025-M Ni; Py , T[b]	-	-	-	-	129.
0.0025-M Ni; Py , T[a,b]	-	-	-	-	46.3
0.0005-M Ni; Py , T[b]	-	-	-	-	129.

(continued)

TABLE LX (continued)

Extraction system	Least-squares values		Upper and lower 95 percent confidence limits		Value of K' used to calculate [P]
	p**	K'	p**	K'	
0.005-M Ni; 3-Pic , T^a	43.0	64.6	46.2 , 39.8	46.7 , 85.4	64.6
0.005-M Ni; 4-Pic , T^a	33.0	98.3	35.2 , 30.8	80.0 , 119.	98.3
0.005-M Zn; Py , T	13.3	11.8	13.53 , 13.07	8.2 , 15.4	11.8
0.005-M Zn; Py , T^a	13.6	7.2	13.76 , 13.44	4.8 , 9.6	7.2
0.005-M Zn; 3-Pic , T^a	54.5	9.7	57.5 , 51.5	< 0 , 21.7	9.7
0.005-M Zn; 4-Pic , T^a	51.0	< 0	56.6 , 45.4	< 0 , 18.1	0
0.001-M Co; Py , T	13.5	35.5	13.62 , 13.38	28.2 , 43.0	35.5
0.001-M Co; Py , T^a	14.2	< 0	14.32 , 14.08	< 0 , 1.1	0
0.001-M Co; 3-Pic , T^a	58.0	< 0	59.8 , 56.2	< 0 , 14.2	0
0.001-M Co; 3-Pic , T^a	50.5	< 0	51.9 , 49.1	< 0 , 8.2	0

NOTES: (1) T means thiocyanate. The concentration of metal quoted is the initial value for the aqueous phase, before equilibration.

(2) Py = pyridine; Pic = picoline.

(3) For the definition of K' see equation (36); for its calculation, see equation (41).

(4) For the determination of the least-squares values and the 95 percent confidence limits, see Appendix XVI.

(5) The superscript "a" denotes extractions made in the presence of added pyridinium or picolinium chloride.

(6) The superscript "b" denotes extractions made into benzene.

It is shown in Appendix XVIIIA that complexes of the type MP_r ($r = 1, 2, 3 \ldots$) would not alone account for the observed decrease in the partition coefficient of the free ligand in the presence of a metal and thiocyanate by combining with some of the pyridine (or picoline). Therefore a mixed complex is postulated. The most predominant of the metal-pyridine (or metal picoline) complexes was shown to be the monopyridinate (or monopicolinate). Therefore, it was assumed that the most predominant mixed complex would also be a monopyridinate (or monopicolinate).

2. Calculation of Free Pyridine (or Picoline) Concentrations in the Aqueous Phases of the Metal Pyridine and Picoline Thiocyanate Extraction Systems

The total equilibrium concentrations of metal, pyridine (or picoline) and thiocyanate in the aqueous phase of each metal pyridine and picoline thiocyanate extraction system were known.

The concentration of free pyridine (or picoline) in the aqueous phase, $[P]$, was obtained from the relationship:

$$[P] = [P]_{T,A} - [P]_b \qquad (27)$$

However, this calculation required the evaluation of $[P]_b$, the concentration of bound pyridine (or picoline) in the aqueous phase.

Since monopyridine (or monopicoline) complexes (mixed and otherwise) have been proposed as the predominant species of pyridine (or picoline) complexes in the aqueous phase, then equation (28) may be written as

$$[P]_b = \sum_{n=0} [M][P][T]^n K_{1,n} \qquad (33)$$

Moreover, for an aqueous solution that does not contain significant amounts of the pure and mixed multipyridinates (or multipicolinates) of the metal, the concentration of free metal in the aqueous phase is given by

$$[M] = \frac{[M]_{T,A}}{\sum_{n=o} K_{o,n} [T]^n + \sum_{n=o} [P] [T]^n K_{1,n}} \qquad (34)$$

where $[M]_{T,A}$ is the total concentration of metal in the aqueous phase, $K_{o,n}$ is the overall formation constant in aqueous solution of the n^{th} metal thiocyanate complex ($K_{o,n} = 1$ for $n = o$), and $K_{1,n}$ is the overall formation constant of the n^{th} metal pyridine (or picoline) thiocyanate complex ($K_{1,n} \neq o$ for $n = o$). Since the concentration of free thiocyanate, $[T]$, was maintained essentially constant* in the aqueous phase of every extraction experiment, then equations (33) and (34) give

$$[P]_b = \frac{[M]_{T,A} [P] K'}{1 + [P] K'} \qquad (35)$$

where

$$K' = \frac{\sum_{n=o} K_{1,n} [T]^n}{\sum_{n=o} K_{o,n} [T]^n} \qquad (36)$$

From equations (27) and (35),

$$[P] = [P]_{T,A} - \frac{[M]_{T,A} [P] K'}{1 + [P] K'} \qquad (37)$$

It is evident that, provided K' can be evaluated, equation (37) provides a means of evaluating $[P]$, the concentration of free pyridine (or picoline) in the aqueous phase. It proved possible to obtain K' by the method described below:

---

* This constancy is affirmed by the data in Appendix XVIIIB.

The apparent partition coefficient, p*, has been defined by equation (23); it may be written in terms of different parameters. Thus

$$p^* = \frac{[P]_o + [P]_l}{[P]_{T,A}} \tag{38}$$

where $[P]_{T,A}$ is the total concentration of pyridine (or picoline) in the aqueous phase, and $[P]_o$ and $[P]_l$ are, respectively, the concentrations of free and loosely-bonded* pyridine (or picoline) in the organic phase.

Another form of partition coefficient, p_t, was defined as follows:

$$p_t = \frac{[P]_o + [P]_l}{[P]} \tag{39}$$

where $[P]$ is the concentration of free pyridine (or picoline) in the aqueous phase.

Combination of equations (37), (38) and (39) gives

$$\frac{p_t - p^*}{p^*} = \frac{[M]_{T,A}\ K'}{1 + [P]\ K'} \tag{40}$$

from which

$$\lim_{[P]_{T,A} \to 0} \frac{p_t - p^*}{p^*} = \frac{p - p^{**}}{p^{**}} = [M]_{T,A}\ K' \tag{41}$$

where p** has been defined by equation (32), and tabulated in Table LX. From the known values of p, p** and $[M]_{T,A}$ for each of the specified metal pyridine and picoline thiocyanate extraction systems, the corresponding values of K' were computed. They are given in Table LX, together with

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* "Loosely-bonded" designates pyridine not bonded directly (through the nitrogen atom) to the central metal ion, but nevertheless associated with the metal pyridine thiocyanate complex in the organic phase.

their 95% confidence limits*.

A range of initial metal concentrations was used in the nickel and cobalt pyridine thiocyanate extraction systems. For these systems, independent estimates of K' were obtained; they are also in Table LX.

From the values of K' the sought-for values of $[P]$ for each extraction system were calculated by using equation (37) and the experimental values of $[M]_{T,A}$ and $[P]_{T,A}$. These experimental data, together with the computed values for $[P]$ are in Appendix XVI. The values of $[P]$ are required in later sections.

Only a few experiments were carried out during the study of the distribution of nickel pyridine thiocyanate between benzene and 0.3-M potassium thiocyanate. The concentration of free pyridine was found by using a value for K' of 129 or 46.3**; these values had been found from the distribution of nickel pyridine thiocyanate between chloroform and aqueous 0.3-M potassium thiocyanate solution, where more data were available.

Where K' had been found for a range of initial metal concentrations (cobalt and nickel pyridine thiocyanate extraction systems), the value found in the case of the highest metal concentration (0.0025M for cobalt; 0.005M for nickel) was used to calculate $[P]$ for those particular systems; it is seen from the 95 percent confidence limits of K' given in Table LX for these systems that this value of K'

---

* In some cases the "best" value of p** was very slightly greater than p, thereby resulting in a negative value for K'. For these cases, the 95 percent confidence limits of K' always included a value of zero, and a more positive value; the "best" value of K' was then taken to be zero.

** The value of 46.3 was used where pyridinium chloride had been added to the aqueous phase.

was likely to be the most accurate.

A limited study had been made of the cobalt 2-picoline thiocyanate extraction system. The concentrations of free 2-picoline in these extraction experiments were not calculated for the following reasons: (1) a concentration of 2-picoline of 3.67M in the organic phase was required to extract 99.2 percent of the cobalt; over this range (zero to 3.67M) of 2-picoline concentrations it was expected that neither the activity coefficients nor the 2-picoline partition coefficient would remain constant; and (2) because of the high concentration of 2-picoline in the aqueous phase*, it was expected that only a small proportion of it (less than one percent) would be complexed. Therefore, the total concentration of 2-picoline in the aqueous phase was a good approximation to the free 2-picoline concentration of that phase.

3. Calculation of Stepwise Formation Constants in the Organic Phase

The average number of pyridine or picoline ligands, $\bar{n}$, bound to each metal atom in the organic phase was found from the relationship

$$\bar{n} = \frac{[P]_{T,o} - [P]_o}{[M]_{T,o}} \qquad (42)$$

where $[M]_{T,o}$ and $[P]_{T,o}$ are the concentrations of total metal and total pyridine (or picoline), respectively, in the organic phase, and $[P]_o$ is the concentration of free pyridine (or picoline) in the organic phase.

* When 2-picoline was present in the aqueous phase, the ratio of 2-picoline to metal in that phase increased from a value of 1.5 to about 10^4 while the percent extraction increased from 1.52 percent to 99.2 percent (see Table XLVIII).

Dimers of the metal were sought for but not found in the organic phase (see Part V-4-1). Therefore, calculations were based on the metal in the organic phase being present only* as the metal dipyridine (or dipicoline) thiocyanate, $[MP_2T_2]_o$, and the metal tetrapyridine (or tetrapicoline) thiocyanate, $[MP_4T_2]_o$.

Therefore

$$\bar{n} = \frac{2[MP_2T_2]_o + 4[MP_4T_2]_o}{[MP_2T_2]_o + [MP_4T_2]_o} \qquad (43)$$

For the following equilibrium in the organic phase:

$$MP_2T_2 + 2P = MP_4T_2 ,$$

$$k_4 = \frac{[MP_4T_2]_o}{[MP_2T_2]_o [P]_o^2} \qquad (44)$$

whence

$$z = \frac{\bar{n} - 2}{4 - \bar{n}} = k_4 [P]_o^2 \qquad (45)$$

A plot of z against $[P]_o^2$ should give a straight line with slope k_4. In practice, z versus $[P]_o^2$ was convenient when the dipyridinate (or dipicolinate) was the predominant species, and z^{-1} versus $[P]_o^{-2}$ was convenient when the tetrapyridinate was predominant.

The calculations are in Appendix XVII, as are the detailed results. In summary the results are as follows: (1) the pyridine, 3-picoline and 4-picoline thiocyanates of cobalt, nickel and cadmium are

---

* It has been shown in Part V-3 that the metal thiocyanates themselves were not measurably extracted in the absence of pyridine (or picoline). The metal thiocyanate concentration in the organic phase may therefore be ignored. It is concluded in Part VII that the organic phase contained only metal dipyridine (or dipicoline) thiocyanates and metal tetrapyridine (or tetrapicoline) thiocyanates.

present in the organic phase almost exclusively as the metal tetrapyridine and tetrapicoline thiocyanates; and (2) the pyridine, 3-picoline and 4-picoline thiocyanates of zinc are present in the organic phase almost exclusively as the metal dipyridine and dipicoline thiocyanates.

The preponderance of one complex species in the organic phase made impossible the calculation of a useful value for k_4. Qualitatively, the results are useful, and they are confirmed in a later section by an independent method.

4. Estimation of the Product of the Partition Coefficient of the Metal Pyridine (or Picoline) Thiocyanate Complex and the Overall Formation Constant of the Complex in the Aqueous Phase

It has been shown in Part V-4-1 that the existence of polynuclear species in the organic phase was unlikely. Therefore the distribution ratio, D, of the metal between the aqueous and organic phases is given by

$$D = \frac{[MP_2T_2]_o + [MP_4T_2]_o}{\sum_{m=o} \sum_{n=o} [MP_mT_n]} \qquad (46)$$

where $[MP_2T_2]_o$ and $[MP_4T_2]_o$ represent the concentrations, in the organic phase, of metal dipyridine (or dipicoline) thiocyanate and metal tetrapyridine (or tetrapicoline) thiocyanate respectively, and $[MP_mT_n]$ represents the concentration of every mononuclear metal species in the aqueous phase.

It will be assumed that the activity coefficients remain nearly constant* throughout the range of concentrations used.

---

* Since the extraction of each metal pyridine and picoline thiocyanate was made from an aqueous medium of nearly-constant ionic strength

(footnote continued)

The partition coefficients of the extractable metal complexes now are given by

$$p_2 = \frac{[MP_2T_2]_o}{[MP_2T_2]} \tag{47}$$

and

$$p_4 = \frac{[MP_4T_2]_o}{[MP_4T_2]} \tag{48}$$

The formation constant, $K_{m,n}$, of each mononuclear metal pyridine (or picoline) thiocyanate species in the aqueous phase is given by

$$K_{m,n} = \frac{[MP_mT_n]}{[M][P]^m[T]^n} \tag{49}$$

and so

$$D = \frac{p_2 K_{2,2} (1 + B[P]^2)[P]^2[T]^2}{\sum_{m=o} \sum_{n=o} K_{m,n}[P]^m[T]^n} \tag{50}$$

where

$$B = \frac{p_4 K_{4,2}}{p_2 K_{2,2}} \tag{51}$$

---

* (0.3-M potassium thiocyanate), it was expected that the activity coefficients of all species in the aqueous phase would remain almost constant. The activity coefficients of metal pyridine and picoline thiocyanate complexes in chloroform (or in benzene) have not been reported; for the purposes of the present section, the activity coefficients of these species were assumed to remain constant, and to have values very near unity.

Equation (50) reduces to

$$D = \frac{p_2 K_{2,2} (1 + B[P]^2) [P]^2}{A + f[P]} \tag{52}$$

where

$$A = \sum_{n=0} K_{o,n} [T]^{n-2} \tag{53}$$

and

$$f[P] = \sum_{m=1} K_{m,o} [P]^m [T]^{-2} + \sum_{r=1} K_{r,1} [P]^r [T]^{-1} + \ldots \tag{54}$$

It may readily be shown that equation (52) then leads to

$$\left(\frac{\partial \log D}{\partial \log [P]} \right)_{[T]} = 2 + R_1 - R_2 \tag{55}$$

where

$$R_1 = \frac{2 B[P]^2}{1 + B[P]^2} \tag{56}$$

and

$$R_2 = \frac{[P] f'[P]}{A + f[P]} \tag{57}$$

where $f'[P]$ is the partial derivative of $f[P]$ with respect to $[P]$.

It is evident that R_1 increases from a value of zero to a maximum value of two as $[P]$ increases.

It is shown in Appendix XVIIID that

$$R_2 = \frac{[P]\, K'}{1 + [P]\, K'} \qquad (58)$$

where K' is a constant defined by equation (36).

It is evident from equation (58) that R_2 increases from a value of zero to a maximum value of unity as $[P]$ increases.

It therefore follows that a plot of log D versus log $[P]$ will have a minimum slope of two* and a maximum slope of four. In between these limits of slope there will be curvature.

In Figs. 47 to 50, plots are given for log D versus log $[P]$, at constant thiocyanate concentration, for the various metal pyridine and picoline thiocyanate extraction systems studied. It is seen that the curves are apparently linear from the smallest value of log $[P]$ up to nearly the largest value of log $[P]$. The slope of the linear portion of each curve is in Table LXI. The slopes for the pyridine, 3-picoline and 4-picoline thiocyanates of cobalt, nickel and cadmium were each four; those for the pyridine, 3-picoline and 4-picoline thiocyanates of zinc and the 2-picoline thiocyanate of cobalt were each two.

These observations made it clear that, over the entire range of free pyridine (or picoline) concentrations used in the present investigation the value of R_1 was (i) very close to two for the cobalt, nickel and cadmium pyridine (3-picoline and 4-picoline) thiocyanate systems; and (ii) very close to zero for the cobalt 2-picoline thiocyanate system and for the zinc pyridine, 3-picoline and 4-picoline thiocyanate systems.

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* If R_1 is near zero for all pyridine (or picoline) concentrations, then a plot of log D versus log $[P]$ may have a minimum slope of unity.

FIGURES 47 to 50

The logarithm of the distribution ratio of the metal, log D, versus the logarithm of the free pyridine (or picoline) concentration in the aqueous phase, log [P], for each of the metal pyridine and picoline thiocyanate extraction systems.

NOTES: (1) The data for these graphs are in Appendix XVI.

(2) All metal concentrations specified in the Figures are the values initially present in the aqueous phase, before equilibration.

(3) The system was chloroform in equilibrium with a 0.3-M aqueous solution of potassium thiocyanate, containing metal ion and pyridine (or picoline) at 25.0°C. In one case benzene replaced chloroform.

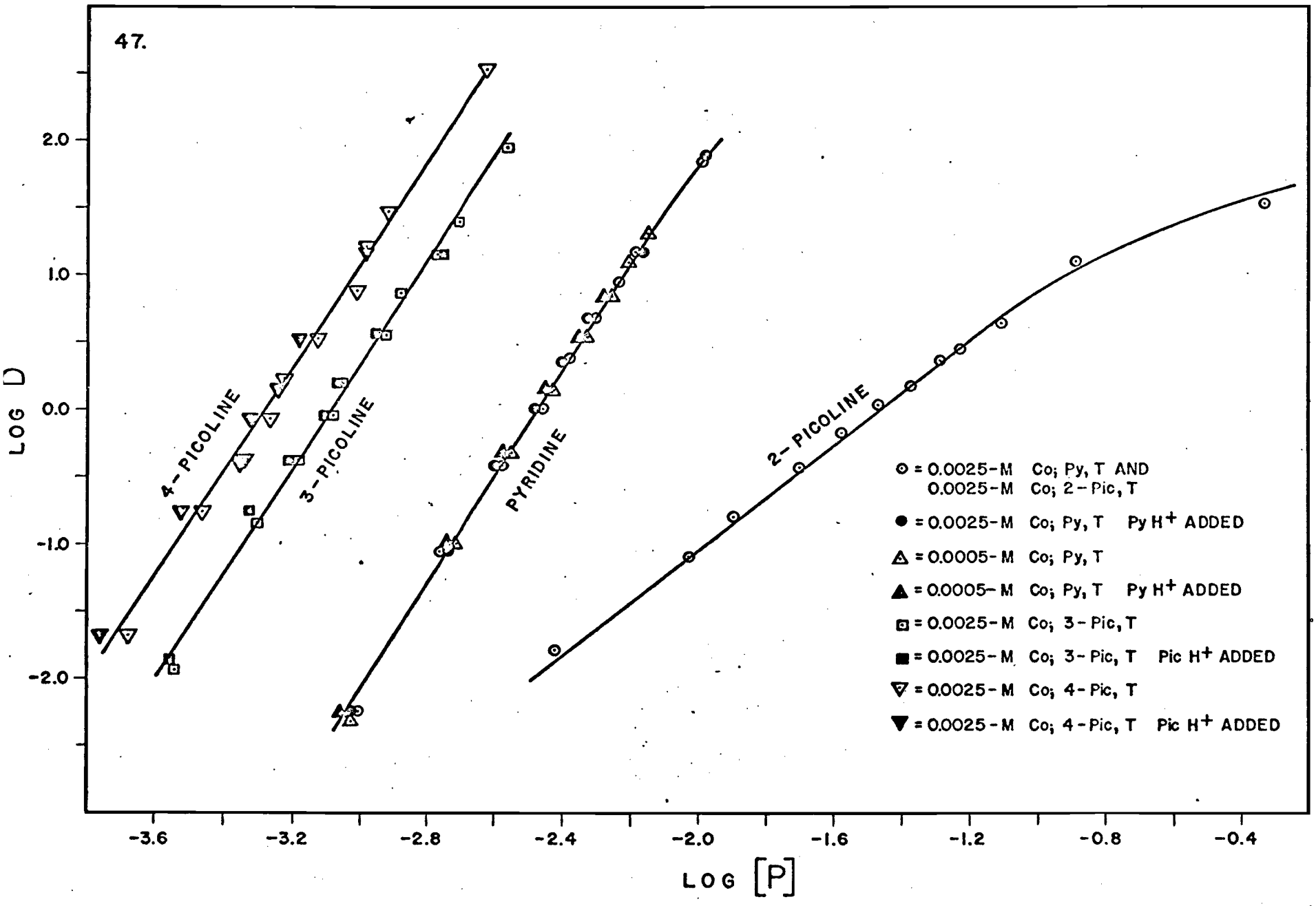
LEGEND: Py = pyridine

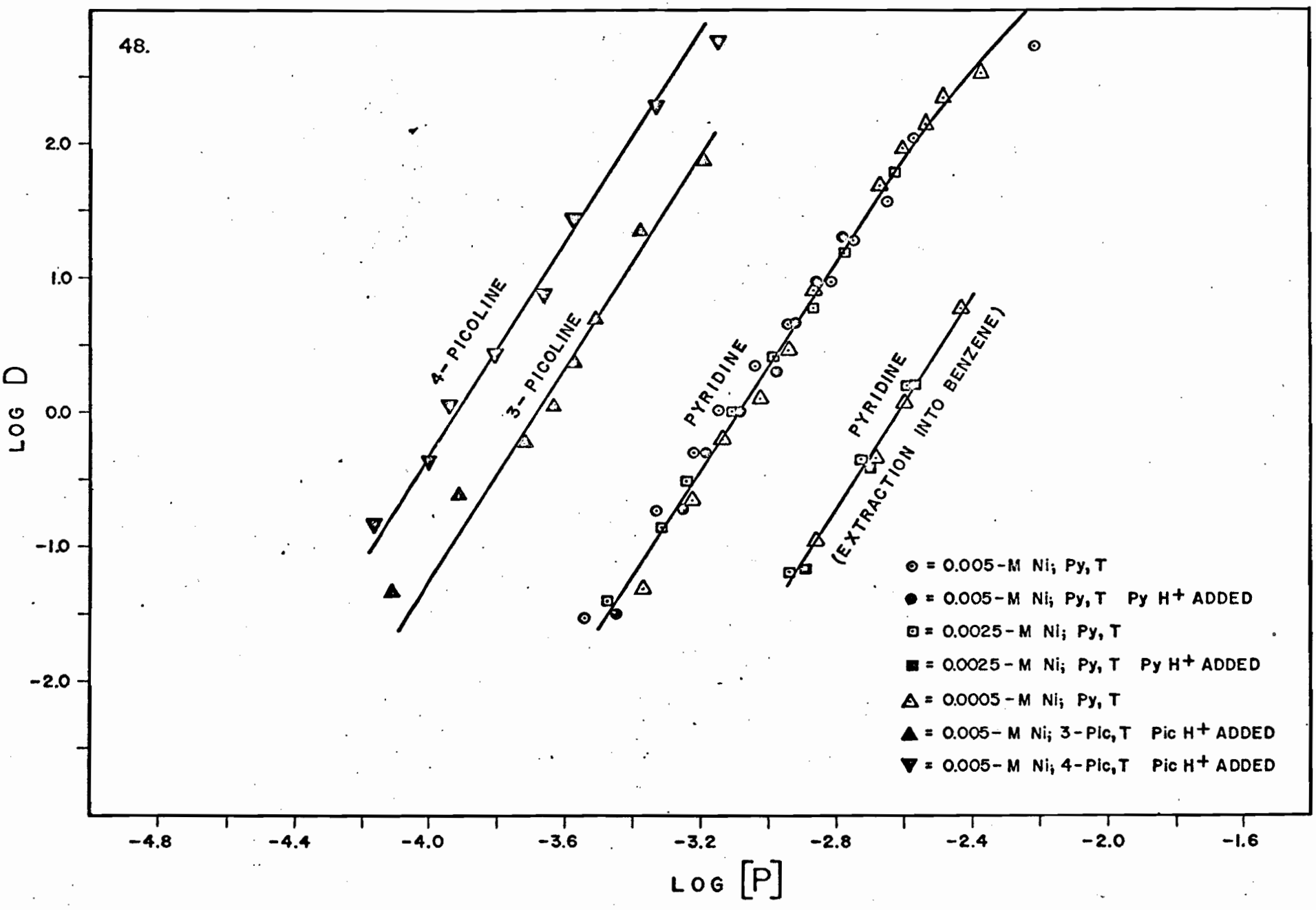
PyH^+ = pyridinium ion

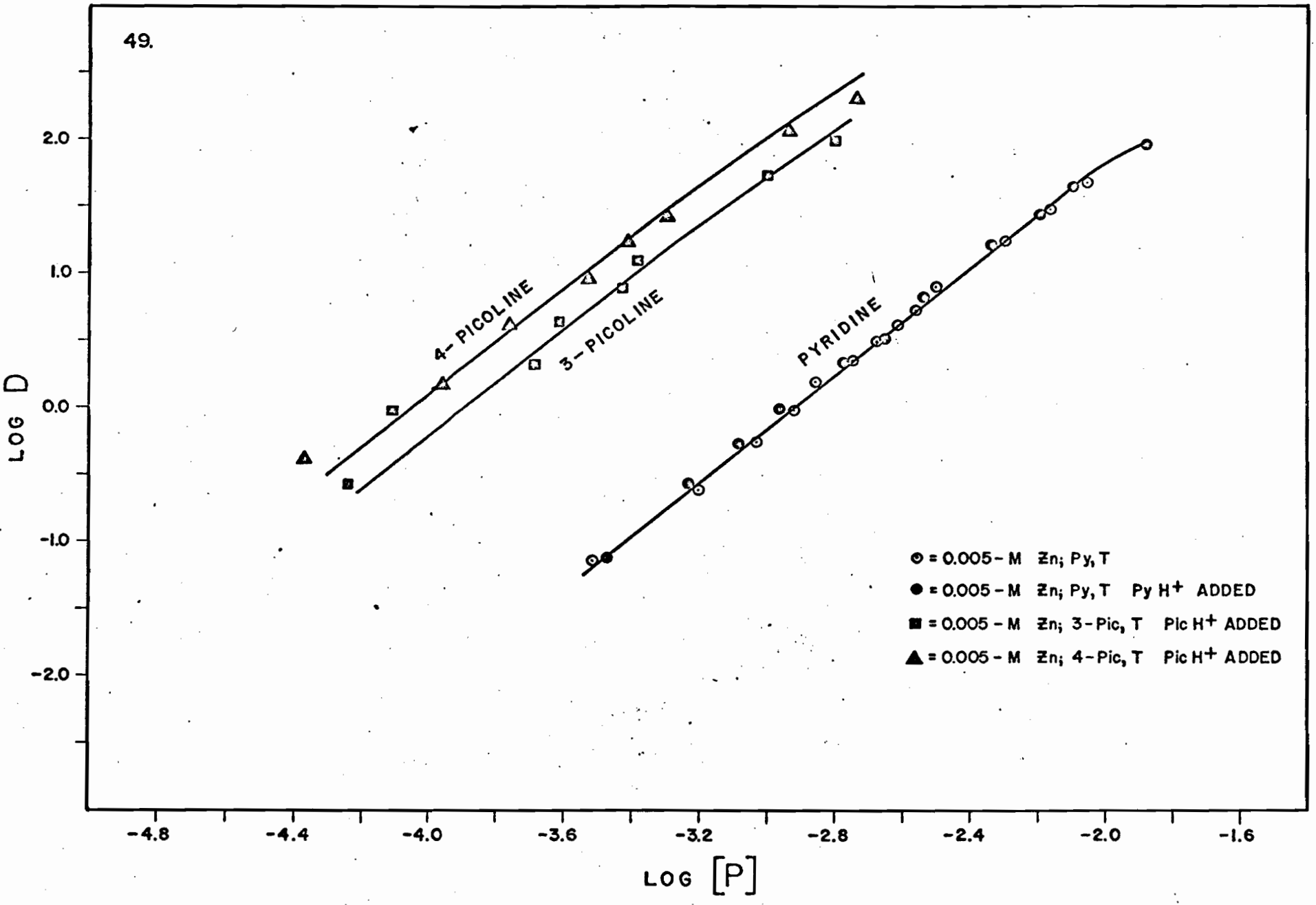
Pic = picoline

$PicH^+$ = picolinium ion

T = thiocyanate


LOG D
LOG [P]
2.0
1.0
0.0
-1.0
-2.0
-3.6
-3.2
-2.8
-2.4
-2.0
-1.6
-1.2
-0.8
-0.4
4-PICOLINE
3-PICOLINE
PYRIDINE
2-PICOLINE
⊙ = 0.0025-M Co; Py, T AND 0.0025-M Co; 2-Pic, T
● = 0.0025-M Co; Py, T Py H+ ADDED
△ = 0.0005-M Co; Py, T
▲ = 0.0005-M Co; Py, T Py H+ ADDED
⊡ = 0.0025-M Co; 3-Pic, T
■ = 0.0025-M Co; 3-Pic, T Pic H+ ADDED
▽ = 0.0025-M Co; 4-Pic, T
▼ = 0.0025-M Co; 4-Pic, T Pic H+ ADDED


48.
LOG D
2.0
1.0
0.0
-1.0
-2.0
-4.8
-4.4
-4.0
-3.6
-3.2
-2.8
-2.4
-2.0
-1.6
LOG [P]
4-PICOLINE
3-PICOLINE
PYRIDINE
PYRIDINE
(EXTRACTION INTO BENZENE)
⊙ = 0.005-M Ni; Py, T
● = 0.005-M Ni; Py, T Py H+ ADDED
⊡ = 0.0025-M Ni; Py, T
■ = 0.0025-M Ni; Py, T Py H+ ADDED
△ = 0.0005-M Ni; Py, T
▲ = 0.005-M Ni; 3-Pic, T Pic H+ ADDED
▼ = 0.005-M Ni; 4-Pic, T Pic H+ ADDED


4-PICOLINE
3-PICOLINE
PYRIDINE
⊙ = 0.005-M Zn; Py, T
● = 0.005-M Zn; Py, T Py H+ ADDED
■ = 0.005-M Zn; 3-Pic, T Pic H+ ADDED
▲ = 0.005-M Zn; 4-Pic, T Pic H+ ADDED
LOG D
LOG [P]
2.0
1.0
0.0
-1.0
-2.0
-4.8
-4.4
-4.0
-3.6
-3.2
-2.8
-2.4
-2.0
-1.6

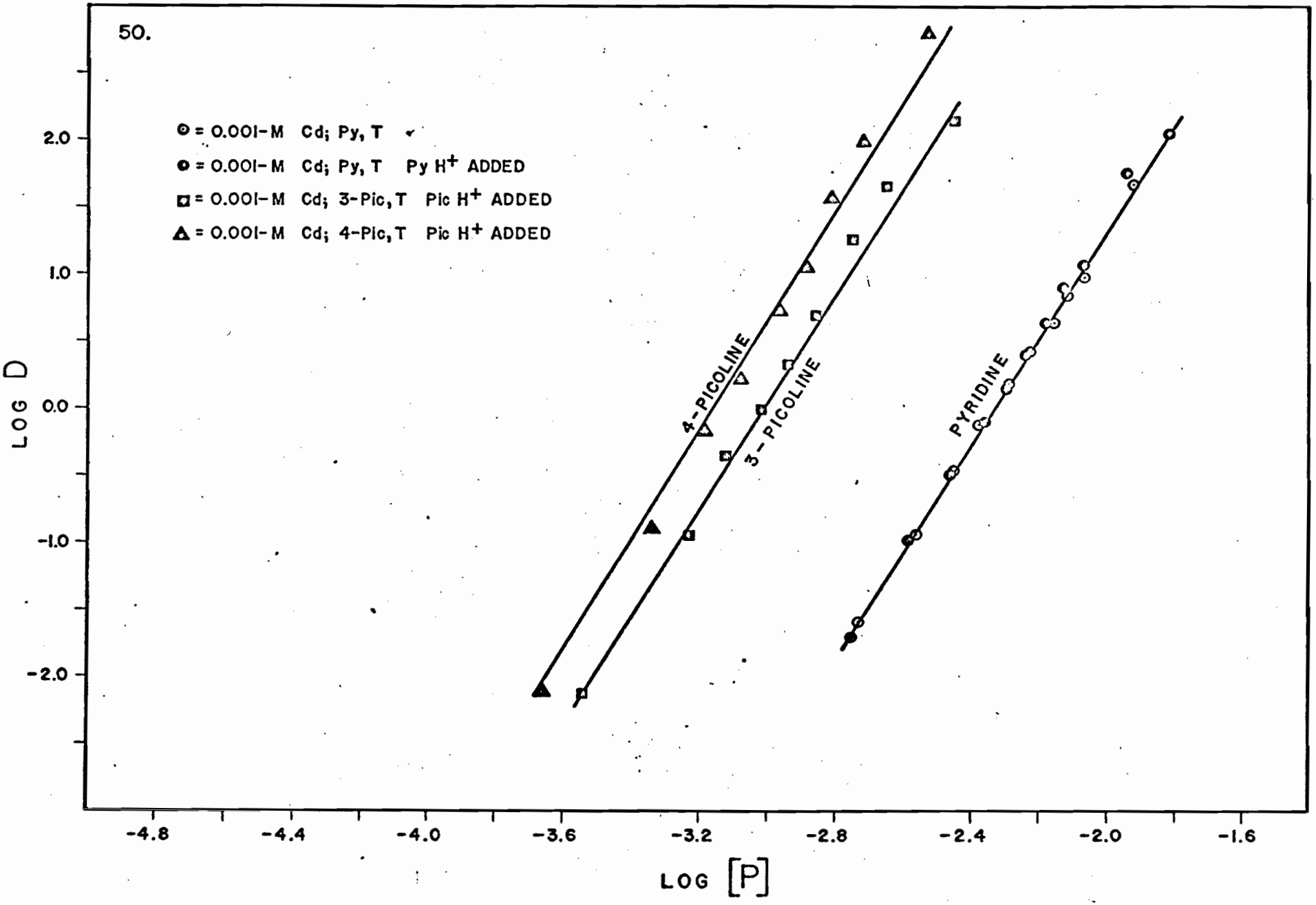

⊙ = 0.001-M Cd; Py, T
● = 0.001-M Cd; Py, T Py H+ ADDED
□ = 0.001-M Cd; 3-Pic, T Pic H+ ADDED
△ = 0.001-M Cd; 4-Pic, T Pic H+ ADDED
4-PICOLINE
3-PICOLINE
PYRIDINE
LOG D
LOG [P]
2.0
1.0
0.0
-1.0
-2.0
-4.8
-4.4
-4.0
-3.6
-3.2
-2.8
-2.4
-2.0
-1.6

TABLE LXI

Apparent slope of the line log D versus log [P] (from Figs. 47 to 50) for the metal pyridine and picoline thiocyanate extraction systems (in chloroform) at 25.0°C

Metal (II)	Ligand	Apparent slope of log D versus log [P]
Cobalt	Pyridine	4.00
	2-Picoline	1.96
	3-Picoline	3.93
	4-Picoline	3.98
Nickel	Pyridine	3.95
	Pyridine*	3.98
	3-Picoline	3.97
	4-Picoline	3.98
Zinc	Pyridine	2.00
	3-Picoline	1.99
	4-Picoline	1.99
Cadmium	Pyridine	4.00
	3-Picoline	4.00
	4-Picoline	4.02

*Extraction into benzene.

However, at the highest values of log [P] for some extraction systems the slope of the curve was somewhat less than four, or less than two. This reduction in slope is due to the significant contribution of R_2 at these higher concentrations of free pyridine (or picoline). In Fig. 51, plots are given of R_2 versus log [P] at different values of K'. It is seen, for example, that at a pyridine (or picoline) concentration of 10^{-2}M (log [P] = -2.0), R_2 has a value of zero or 0.2 corresponding to a K' value of zero or 25, respectively. Therefore, when K' is 25 a plot of log D versus log [P] should have a slope of about 3.8 at a pyridine (or picoline) concentration of 10^{-2}M.; this is approximately the slope observed at 10^{-2}M pyridine for the cobalt pyridine thiocyanate extraction system (K' = 23.3; see Table LX).

For the case where R_1 has a value near two, then the ratio B, as defined by equation (51), is much greater than $[P]^{-2}$. Equation (52) may now be written as

$$\log p_4 K_{4,2} = \log D - 4 \log [P] + \log (A + f[P]) \qquad (59)$$

For the case where R_1 has a value near zero, then the ratio B is much smaller than $[P]^{-2}$. Equation (52) may now be written as

$$\log p_2 K_{2,2} = \log D - 2 \log [P] + \log (A + f[P]) \qquad (60)$$

It is shown in Appendix XVIIID that

$$f[P] = [P] K'A \qquad (61)$$

FIGURE 51

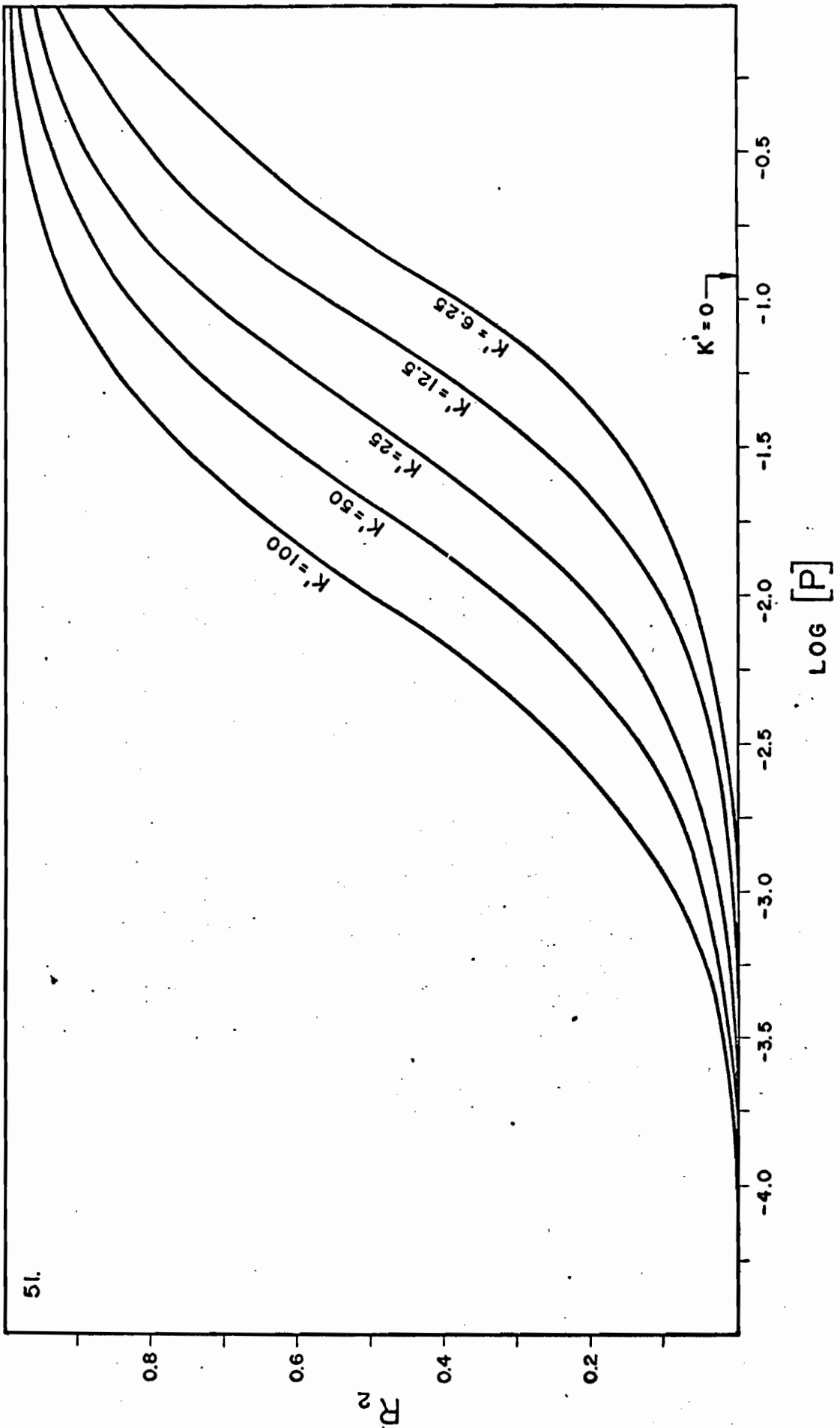
Plots of R_2 versus log $[P]$ for different values of K'

NOTES: (1) R_2 was calculated from equation (58):

$$R_2 = \frac{[P]\,K'}{1 + [P]\,K'}$$

(2) K' is a constant defined by equation (36).

(3) $[P]$ is the free pyridine (or picoline) concentration in the aqueous phase.


51.
R_2
0.2
0.4
0.6
0.8
LOG [P]
-4.0
-3.5
-3.0
-2.5
-2.0
-1.5
-1.0
-0.5
K'=0
K'=6.25
K'=12.5
K'=25
K'=50
K'=100

Equations (59) and (60), respectively, are now written as

$$\log p_4 K_{4,2} = \log D - 4 \log [P] + \log A + \log(1 + [P] K') \quad (62)$$

and

$$\log p_2 K_{2,2} = \log D - 2 \log [P] + \log A + \log(1 + [P] K') \quad (63)$$

The values of log D, log [P], [P] and K' were known for each metal pyridine and picoline thiocyanate extraction system; they are tabulated in Appendix XVI. The values of log A have been computed* and tabulated in Appendix XVIIIC. For each** extraction system, these values were used to compute $p_2 K_{2,2}$ (or $p_4 K_{4,2}$) for each extraction experiment. The mean value of $p_2 K_{2,2}$ (or $p_4 K_{4,2}$) and its standard deviation then were computed for each of the metal pyridine and picoline thiocyanate extraction systems. The results are in Table LXII.

A statistical analysis*** of the data was then made. Thus it was found that the mean values of $p_4 K_{4,2}$ (or $p_2 K_{2,2}$) were not significantly different (1) when the initial concentration of metal was varied for either the extraction of cobalt or nickel pyridine thiocyanate

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* It is shown in Appendix XVIIIC that if the concentration of free thiocyanate in the aqueous phase is varied by ± 2 percent, the distribution ratio will vary by only ± 1 percent.

** For reasons discussed previously, K' had not been evaluated for the cobalt 2-picoline thiocyanate system. Therefore f[P] could not be evaluated at all the experimental points. To obtain an estimate of $p_2 K_{2,2}$ for this system, the value of log [P] was read from the graph (Fig. 47) at log D = 0 (the approximate mid-point of the curve). Then $p_2 K_{2,2}$ was found from the equation

$$\log p_2 K_{2,2} = \log A - 2 \log [P]$$

*** The t-test of significance (63) for the difference between means was used.

TABLE LXII

Mean value and standard deviation, s_x, of the product $p_2 K_{2,2}$ (or $p_4 K_{4,2}$) for each of the metal pyridine and picoline thiocyanate extraction systems at 25.0°C

Extraction system	$p_2 K_{2,2}$	s_x	$p_4 K_{4,2}$	s_x	Composite mean value	
					$p_2 K_{2,2}$	$p_4 K_{4,2}$
0.0025-M Co; Py , T	-		8.96×10^{11}	0.85×10^{11}		
0.0025-M Co; Py , T[a]	-		8.75×10^{11}	0.84×10^{11}		9.02×10^{11}
0.0005-M Co; Py , T	-		9.08×10^{11}	0.84×10^{11}		
0.0005-M Co; Py , T[a]	-		9.43×10^{11}	0.32×10^{11}		
0.0025-M Co; 2-Pic , T	8.51×10^{4}	-		-		
0.0025-M Co; 3-Pic , T	-		2.42×10^{14}	0.40×10^{14}		2.61×10^{14}
0.0025-M Co; 3-Pic , T[a]	-		2.96×10^{14}	0.64×10^{14}		
0.0025-M Co; 4-Pic , T	-		1.29×10^{15}	0.17×10^{15}		1.44×10^{15}
0.0025-M Co; 4-Pic , T[a]	-		1.72×10^{15}	0.38×10^{15}		
0.005-M Ni; Py , T	-		3.82×10^{14}	1.24×10^{14}		
0.005-M Ni; Py , T[a]	-		3.04×10^{14}	0.63×10^{14}		3.42×10^{14}
0.0025-M Ni; Py , T	-		3.42×10^{14}	0.38×10^{14}		
0.0005-M Ni; Py , T	-		3.10×10^{14}	0.65×10^{14}		
0.0025-M Ni; Py , T[b]	-		5.36×10^{12}	0.28×10^{12}		
0.0025-M Ni; Py , T[a,b]	-		3.81×10^{12}	0.37×10^{12}		4.77×10^{12}
0.0005-M Ni; Py , T[b]	-		4.91×10^{12}	0.58×10^{12}		

(continued)

TABLE LXII (continued)

Extraction system	$p_2 K_{2,2}$	s_x	$p_4 K_{4,2}$	s_x	Composite mean value	
					$p_2 K_{2,2}$	$p_4 K_{4,4}$
0.005-M Ni; 3-Pic , T[a]	-		8.87×10^{16}	4.31×10^{16}		
0.005-M Ni; 4-Pic , T[a]	-		5.83×10^{17}	1.98×10^{17}		
0.005-M Zn; Py , T	2.40×10^{7}	0.14×10^{7}	-		2.43×10^{7}	
0.005-M Zn; Py , T[a]	2.48×10^{7}	0.22×10^{7}	-			
0.005-M Zn; 3-Pic , T[a]	2.38×10^{9}	1.05×10^{9}	-			
0.005-M Zn; 4-Pic , T[a]	4.02×10^{9}	1.60×10^{9}	-			
0.001-M Cd; Py , T	-		2.88×10^{11}	0.32×10^{11}		2.76×10^{11}
0.001-M Cd; Py , T[a]	-		2.62×10^{11}	0.31×10^{11}		
0.001-M Cd; 3-Pic , T[a]	-		1.47×10^{14}	0.46×10^{14}		
0.001-M Cd; 4-Pic , T[a]	-		4.95×10^{14}	1.26×10^{14}		

NOTES: (1) T means thiocyanate. The concentration of metal quoted in the initial value for the aqueous phase, before equilibration.

(2) Py = pyridine; Pic = picoline.

(3) For the definitions of p_4, p_2, $K_{4,2}$ and $K_{2,2}$ see equations (47) to (49); for the calculation of the product $p_4 K_{4,2}$ and $p_2 K_{2,2}$ see equations (62) and (63), respectively.

(4) The standard deviation, s_x, was calculated on the basis of N observations and N-1 degrees of freedom.

(5) The superscript "a" denotes extractions made in the presence of added pyridinium or picolinium chloride.

(6) The superscript "b" denotes extractions made into benzene.

(7) The basic data for the calculations are in Appendix XVI.

into chloroform, or for the extraction of nickel pyridine thiocyanate into benzene; (2) when pyridinium chloride was either present or absent during the extraction of cobalt, nickel, zinc and cadmium pyridine thiocyanates into chloroform; and (3) when picolinium chloride was either present or absent during the extraction of cobalt 3-picoline thiocyanate into chloroform. Only for the extractions of nickel pyridine thiocyanate into benzene and cobalt 4-picoline thiocyanate into chloroform were the mean values of $p_4 K_{4,2}$ found to be different in the presence of added pyridinium and picolinium chloride, respectively; in the former case, the presence of added pyridinium chloride resulted in a smaller value of $p_4 K_{4,2}$; in the latter case, the presence of added picolinium chloride resulted in a larger value of $p_4 K_{4,2}$. The former case was not taken to be significant for the following reasons: (1) the statistically-different value of $p_4 K_{4,2}$ was based on only 5 observations; and (2) pyridinium chloride had no measurable effect on the mean value of $p_4 K_{4,2}$ for the extraction of nickel pyridine thiocyanate into chloroform where many more data were available. The latter case was not taken to be significant for the following reasons: (1) the different value of $p_4 K_{4,2}$ was only barely significant at the 5 percent level (2-tailed test) and not at the 5 percent point (one-tailed test); and (2) this different value of $p_4 K_{4,2}$ could reasonably be attributed to chance.

It was concluded that neither the initial concentration of metal in an extraction system nor the presence of added pyridinium or picolinium chloride in the aqueous phase had any significant effect upon the computed value of $p_4 K_{4,2}$ or $p_2 K_{2,2}$ for that extraction system. It follows that a plot of log D versus log $[P]$ for a given extraction system is independent both of the metal concentration in that extraction

system and of the presence or absence of added pyridinium (or picolinium) chloride in the aqueous phase.

As noted in Part V-4-1, a reduction in the initial concentration of metal in the cobalt and nickel pyridine thiocyanate extraction systems resulted in a small displacement of the sigmoid distribution curve to lower pyridine concentration. For these distribution curves, the distribution ratio, D, was plotted against the total concentration of pyridine in the aqueous phase $[P]_{T,A}$. It is clear from the data in Figs. 47 and 48 for these extraction systems, and from the preceding discussion, that a plot of D versus $[P]$, the concentration of free pyridine in the aqueous phase, would reveal no such displacements in the curves. These displacements may therefore be attributed to complexed pyridine in the aqueous phase.

The addition of pyridinium (or picolinium) chloride to a given extraction system also resulted in a small displacement of the sigmoid distribution curve to lower pyridine (or picoline) concentration. This effect was noticed (see Part V-4-1) in the cobalt, nickel, zinc and cadmium pyridine thiocyanate extraction systems and in the cobalt 3-picoline and 4-picoline thiocyanate systems. However, the reason for this curve displacement remains unexplained even though the computed value of $p_4 K_{4,2}$ is not influenced by the presence or absence of pyridinium (or picolinium) chloride.

Since neither the initial metal concentration in the extraction system nor the presence of pyridinium (or picolinium) chloride in the aqueous phase had any significant effect upon the computed mean value of $p_4 K_{4,2}$ (or $p_2 K_{2,2}$), the composite means were calculated. It was the purpose of the present sub-section to obtain these values and those of

$p_4 K_{4,2}$ or $p_2 K_{2,2}$ found for the other extraction systems. They are discussed in Part VII.

PART VII

DISCUSSION OF RESULTS

1. Introduction

In the present work, all extractions of the metal pyridine and picoline thiocyanates into chloroform (and, in the case of nickel pyridine thiocyanate, into benzene) were from aqueous solutions of nearly-constant ionic strength. This medium was provided by 0.3-M potassium thiocyanate. It was therefore expected that the activity coefficients of all species in the aqueous phase would have remained constant throughout the range of concentrations used, thus making it possible to express the law of mass action in terms of concentrations.

It was shown in Part VI that for the present solvent-extraction systems, the distribution ratio of a metal between the two almost-immiscible phases was a function of the equilibrium concentration of free pyridine (or picoline) in the aqueous phase. Further, this function contained constants characteristic of the particular metal pyridine (or picoline) thiocyanate.

The purposes of the present Section are to interpret the extraction results, and to indicate their use in analytical chemistry.

1-1. Nature of the Extracted Metal Complexes

(a) Experimental Considerations

It was shown in Part V-3-4 that the metal pyridine and picoline thiocyanates, but not the corresponding chlorides, were extracted into the organic phase of the specified solvent-extraction system. It was also shown there that neither the metal thiocyanates nor the metal chlorides were themselves measurably extracted into chloroform. In Part V-4, experiments were reported which established that the molar ratio of thiocyanate to metal in the organic phase was always twice unity.

In Part VI it was concluded that either two or four pyridine (or picoline) ligands were bonded to each metal thiocyanate molecule in the organic phase. Mono-, tri-, penta-, and higher pyridinates (or picolinates) of these transition-metal thiocyanates (cobalt, nickel, zinc and cadmium) in either chloroform or benzene were not found in the present investigation, nor have such species been reported in the chemical literature. Finally, the experimental work of the present investigation showed that dimers and higher aggregates of the metal complexes were absent in measurable amounts from the organic phase, over the concentration range studied.

From the above observations it was concluded that the metal was present in significant amounts in the organic phase only as the metal dithiocyanate to which were bonded either two or four pyridine (or picoline) ligands.

Since cobalt-ammine complexes are known to be readily oxidized by molecular oxygen both in aqueous (120) and non-aqueous (121) solutions, it was considered possible for the extraction systems containing cobalt that some of the metal had been oxidized to the tervalent state. However, experimental evidence was presented in Part V-3-2 which established that equilibrium was attained within 10 seconds of mechanical shaking for the cobalt pyridine thiocyanate extraction system; it is unlikely that, for a molecular process such as the oxidation of divalent cobalt, equilibrium would be attained so rapidly. In addition, it was shown in Part V-4-2, that when pyridinium chloride was added to two extraction experiments which were otherwise identical, the distribution ratio of cobalt was not changed although the pH of the aqueous phase was lowered considerably (compare, for example, the data

in Tables LA and LIIA). Moreover this same effect was noted for the other metals (nickel, zinc and cadmium). On the basis of this additional evidence it was concluded that tervalent cobalt was absent from the aqueous phase. Finally, it has been found (119) that the overall formation constant of cobalt tetrapyridine thiocyanate in benzene at 25°C is the same whether or not the solvent has been dried, and whether or not the solvent has been purposely aerated or de-aerated.

Ion pairs of the type $(PH^+)_2 [\ Co(NCS)_4^{=}\ ]$, where PH^+ is pyridinium or picolinium ion, were considered unlikely to be present. As evidence, it was shown in Part V-4 that none of the metals was extracted from an aqueous solution containing only the metal, potassium thiocyanate and pyridinium (or picolinium) ion. Additional evidence is presented below.

The possible existence of ion pairs of the type $[\ CoP_4^{++}, Co(NCS)_4^{=}\ ]$ in the organic phase was also considered. However, it was shown in Part VI that, for example, 3.97 ± 0.04 mole of pyridine, 3-picoline or 4-picoline was associated with each mole of cobalt in the organic phase. It may be calculated* that less than 4 percent of the cobalt could be present as such an ion pair. Similarly, it may be calculated that less than 7 percent of the cobalt could be present as $[\ CoP_6^{++}, Co(NCS)_4^{=}\ ]$.

(b) Considerations from Coordination Chemistry

It was concluded in the previous sub-section that the metal complexes in the organic phase were either four- or six coordinated,

* If x is the mole fraction of cobalt present as such an ion pair, then 1-x is the fraction present as cobalt tetrapyridine (or tetrapicoline) thiocyanate. Thus, in the worst case: $2x + 4(1 - x) = 3.93$; $x = 0.035$.

and that each contained two thiocyanate ligands and either two or four pyridine (or picoline) ligands.

Schaffer (72) found from infrared spectra that either end of a thiocyanate ion can bond to a metal ion, but that generally a given metal ion will much prefer one end to the other. Thus, divalent cadmium is the only known example of coordination through either sulphur or nitrogen; divalent cobalt, nickel and zinc are bound to nitrogen. Recent infrared studies by Larsson and Miezis (96) have shown that the thiocyanate ion is bound through nitrogen to the metal in the pyridine thiocyanate complexes of cobalt, nickel, copper, zinc and cadmium.

The pyridine or picoline ligands of the complexes have been shown conclusively by infrared studies (97) to be bound through the nitrogen.

For coordination number six, three geometrical configurations of ligands about the central metal atom are possible; these are planar, octahedral and trigonal-prismatical. Of these, the octahedral arrangement is the most stable (122) since it corresponds to the greatest separation of ligands. Two main types of octahedral metal complexes are recognized. They are outer complexes and inner (penetration) complexes, characterized by bond formation with sp^3d^2 and d^2sp^3 hybrid orbitals of the metal ion, respectively. Since neither zinc nor cadmium have vacant inner d orbitals, only outer complexes are possible. Cobalt and nickel do have vacant inner d orbitals, so inner and outer complexes are possible. However, outer complexes more readily undergo reversible dissociation (122), and so do the metal pyridine and picoline thiocyanates (100,107,108). This suggests that the cobalt and nickel pyridine (and picoline) thiocyanates may be characterized by sp^3d^2 hybrid

orbitals.

For metal complexes with a coordination number of four, the possible configurations are tetrahedral (using sp^3 or sd^3 hybrid orbitals of the metal ion) or square planar (using dsp^2 hybrid orbitals of the metal ion). The choice of arrangement depends upon which orbitals of the metal ion are available. Where d orbitals cannot be used for energy reasons, a tetrahedral configuration is found as, for example, in complexes of divalent zinc and cadmium.

Libus and Uruska (109) have shown from their spectral studies that, in monochlorobenzene solution, the dipyridine chlorides of divalent manganese, cobalt, nickel, copper and zinc are tetrahedral, and the tetrapyridine chlorides are octahedral. Graddon and Watton (100) concluded from a study of magnetic properties and spectra that, in chloroform solution, cobalt complexes of the type $CoP_2(NCS)_2$ and $CoP_4(NCS)_2$, where P = pyridine, 2-picoline*, or 4-picoline, are tetrahedral** and octahedral, respectively. Similar studies by Vallarino and co-workers (108) showed that, in dichloromethane solution, nickel complexes of the type $NiP_2(NCS)_2$ and $NiP_4(NCS)_2$, where P = 2-picoline*, 3-picoline or 4-picoline, are tetrahedral and octahedral, respectively. Nelson and Shepherd (99) showed from magnetic and spectral studies in chloroform solution that nickel complexes of the type $NiP_2(NCS)_2$ and $NiP_4(NCS)_2$, where P = pyridine, 3-picoline or 4-picoline, are tetrahedral and octahedral, respectively.

From these considerations it is concluded that in the low-dielectric solvents chloroform and benzene, the dipyridine (or dipicoline)

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* The tetra-2-picoline thiocyanate could not be formed (100).

** Cobalt dipyridine thiocyanate has been shown to exist as a tetrahedral monomer in nitrobenzene solution (73).

and tetrapyridine (or tetrapicoline) thiocyanates of the transition metals studied had tetrahedral and octahedral configurations, respectively. This conclusion is further supported by the molecular-model studies reported below.

(c) Molecular-Model Studies

Molecular models* of the metal pyridine and picoline thiocyanates were constructed.

For the metal dipyridine and dipicoline thiocyanates it was possible to construct models corresponding to square-planar (cis and trans) arrangements for each of the metal pyridine, 2-picoline, 3-picoline and 4-picoline thiocyanates. However, this square-planar configuration was possible only if the plane of each pyridine or picoline ligand was perpendicular or nearly perpendicular to the thiocyanate-metal-thiocyanate plane (cis) or axis (trans).

For tetrahedral models, steric hindrance was evident only for the 2-picoline complex; this effect could not be avoided by suitable orientation of the 2-picoline molecules. However, tetrahedral rather than square-planar 2-picoline thiocyanates are known to exist in solution (98,100); the present molecular-model evidence suggests that some of the bond distances in these tetrahedra must be somewhat lengthened.

Planar, octahedral and trigonal-prismatical arrangements of ligands are possible for divalent metals of coordination number six. Of these possibilities, only the trans-octahedral** configuration of

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* Courtauld Atomic Models (Griffin and George, Limited, London) were used.

** The trans-octahedral configuration has been reported for the pyridine, 3-picoline and 4-picoline halides of cobalt (110) and nickel (97).

the metal tetrapyridine (or tetrapicoline) thiocyanates could be constructed; this was possible only if the plane of each pyridine or picoline ligand was orientated at approximately 45° to the thiocyanate-metal-thiocyanate axis, to give a propeller-type orientation of the pyridine or picoline ligands. This propeller-type of orientation has been found (111), from crystallographic studies, for nickel tetra-pyridine chloride and bromide. The corresponding cis-configurations apparently are unknown.

Extreme steric effects were evident in models of the 2-picoline complexes. In Part VI it was pointed out that a very high concentration of 2-picoline was required to effect even 50 percent extraction of cobalt 2-picoline thiocyanate into chloroform. Infrared studies have shown that the presence of a methyl group in the 2-position on the pyridine ring prevents the formation of cobalt tetra-2-picoline thiocyanate in either a chloroform solution of 2-picoline (98) or in pure 2-picoline (100). Magnetic and spectral studies have shown (108) that solid nickel tetra-2-picoline thiocyanate does not form. The present molecular-model studies illustrate that steric hindrance is the cause of this marked instability.

The molecular-model studies confirmed the conclusion reached previously, namely that the metal pyridine and picoline thiocyanates would be extracted exclusively as tetrahedral and octahedral complexes.

2. Intercomparison of Extraction Systems

It was shown in Part VI that over the range of pyridine and picoline concentrations used in the present investigation: (a) the pyridine, 3-picoline and 4-picoline thiocyanates of cobalt, nickel and cadmium were extracted almost exclusively as the metal tetrapyridine and tetrapicoline thiocyanates; (b) the zinc pyridine and picoline thiocyanates were extracted mainly as the dipyridine and dipicoline species; and (c) cobalt 2-picoline thiocyanate was extracted mainly as the dipicoline species.

The product of the partition coefficient of the extracted species (p_2 or p_4) and its overall formation constant in the aqueous phase ($K_{2,2}$ or $K_{4,2}$) was also found in Part VI for each of the metal pyridine and picoline thiocyanates; the values found for these products are given in Table LXII, and they have been incorporated into Table LXIII.

The purpose of the present section is to interpret as fully as possible the differences in the values between metals, of this product $p_2 K_{2,2}$ or $p_4 K_{4,2}$. For a given metal complex*, either $p_2 K_{2,2}$ or $p_4 K_{4,2}$ (but not both) had been found in Part VI from experimental data. It was considered useful to try to estimate the value of the unmeasured product $p_2 K_{2,2}$ or $p_4 K_{4,2}$ for the complexes of manganese, cobalt, nickel, copper, zinc and cadmium in the hope of broadening the interpretation of their values. To obtain such estimates the following equation was used:

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* Henceforth this term will refer to a metal pyridine (or picoline) halide or thiocyanate.

TABLE LXIII

Estimated values of k_4, and computed values of $p_2 K_{2,2}$ and $p_4 K_{4,2}$ for the metal pyridine and picoline thiocyanates in chloroform (or benzene) at 25°C

Metal (II)	Ligand	p	k_4	$p_2 K_{2,2}$	$p_4 K_{4,2}$
Manganese	Pyridine	14.1	2.3×10^{5}	-	-
	Pyridine*	2.93	9.0×10^{5}	-	-
	3-Picoline	54.7	7.1×10^{4}	-	-
	4-Picoline	47.2	2.3×10^{5}	-	-
Cobalt	Pyridine	14.1	5.4×10^{4}	8.4×10^{4}	(9.02×10^{11})
	Pyridine*	2.93	2.1×10^{5}	-	-
	2-Picoline	41.2	ca 1.0×10^{-6}	(8.51×10^{4})	1.4×10^{2}
	3-Picoline	54.7	1.7×10^{4}	5.1×10^{6}	(2.61×10^{14})
	4-Picoline	47.2	5.4×10^{4}	1.2×10^{7}	(1.44×10^{15})
Nickel	Pyridine	14.1	4.0×10^{8}	4.3×10^{3}	(3.42×10^{14})
	Pyridine*	2.93	1.6×10^{9}	3.5×10^{2}	(4.77×10^{12})
	3-Picoline	54.7	1.2×10^{8}	2.5×10^{5}	(8.87×10^{16})
	4-Picoline	47.2	4.0×10^{8}	6.5×10^{5}	(5.83×10^{17})
Copper	Pyridine	14.1	6.5×10^{4}	-	-
	Pyridine*	2.93	2.5×10^{5}	-	-
	3-Picoline	54.7	2.0×10^{4}	-	-
	4-Picoline	47.2	6.5×10^{4}	-	-
Zinc	Pyridine	14.1	< 10	(2.43×10^{7})	$< 4.8\times10^{10}$
	Pyridine*	2.93	< 39	-	-
	3-Picoline	54.7	< 3	(2.38×10^{9})	$< 2.1\times10^{13}$
	4-Picoline	47.2	< 10	(4.02×10^{9})	$< 9.0\times10^{13}$

TABLE LXIII (continued)

Metal (II)	Ligand	p	k_4	$p_2 K_{2,2}$	$p_4 K_{4,2}$
Cadmium	Pyridine	14.1	-	-	(2.76×10^{11})
	Pyridine*	2.93	-	-	-
	3-Picoline	54.7	-	-	(1.47×10^{14})
	4-Picoline	47.2	-	-	(4.95×10^{14})

* Extraction into benzene

NOTES: (1) $k_4 = \dfrac{[MP_4T_2]_o}{[MP_2T_2]_o [P]_o^2}$ (see equation (44))

(2) p is the partition coefficient for pyridine (or picoline) between chloroform (or benzene) and 0.3-M potassium thiocyanate solution. Values are from Table LIX.

(3) For definitions of k_4, p_2, p_4, $K_{2,2}$ and $K_{4,2}$, see equations (64) to (66).

(4) Values of $p_2 K_{2,2}$ (or $p_4 K_{4,2}$) given in brackets are from Table LXII. The corresponding values of $p_4 K_{4,2}$ (or $p_2 K_{2,2}$) were computed from equation (64):

$$k_4 = \frac{p_4 K_{4,2}}{p_2 K_{2,2}} \cdot \frac{1}{p^2} \qquad (64)$$

$$k_4 = \frac{p_4 K_{4,2}}{p_2 K_{2,2}} \cdot \frac{1}{p^2} \qquad (64)$$

where

$$k_4 = \frac{[MP_4T_2]_o}{[MP_2T_2]_o [P]_o^2} \qquad (44)$$

p, the partition coefficient of the free ligand (pyridine or picoline) between the organic solvent and 0.3-M potassium thiocyanate solution at 25°C is defined by equation (26):

$$p = \frac{[P]_o}{[P]} \qquad (26)$$

$$p_m = \frac{[MP_mT_2]_o}{[MP_mT_2]} \; ; \quad m = 2, 4 \qquad (65)$$

$$K_{m,2} = \frac{[MP_mT_2]}{[M][P]^m[T]^2} \; ; \; m = 2, 4 \qquad (66)$$

and where the subscript o indicates the organic phase, and absence of a subscript indicates the aqueous phase.

Equation (64) follows at once on combining equations (44), (26), (65) and (66).

The values of p were known for pyridine, 2-picoline, 3-picoline and 4-picoline, and either $p_2 K_{2,2}$ or $p_4 K_{4,2}$ had been measured. Hence in cases where the value of k_4 for a particular metal complex was known, the unmeasured value of $p_2 K_{2,2}$ or $p_4 K_{4,2}$ could be estimated from equation

(64). This was done.

Unfortunately, some necessary data were not available in the literature. In order to evaluate k_4 by using the data available, some assumptions had to be made. A reasonable degree of justification for these assumptions is presented below, but it will be evident that caution is necessary when considering conclusions drawn from the estimates of $p_2 K_{2,2}$ or $p_4 K_{4,2}$. The available literature, and its use in the evaluation of k_4 is next considered.

Libus and Uruska (109) recently reported the stepwise formation constants, k_4, for the tetrapyridine chlorides of divalent manganese, cobalt, nickel, copper and zinc in pure monochlorobenzene at 20°C and 30°C.

King, Koros and Nelson (98) reported the stepwise formation constants for (a) cobalt tetrapyridine chloride, bromide, iodide, cyanate, thiocyanate and selenocyanate; and (b) cobalt tetra-2-picoline thiocyanate, in dried chloroform at 20°C only.

The ratio, r, of the stepwise formation constant, k_4, of cobalt tetrapyridine chloride in chloroform at 20°C to that in monochlorobenzene at 20°C was calculated from the above data (98,109). The value was found to be 1.46. It was then assumed that this value did not vary much when the central metal (cobalt) was changed for manganese, nickel, copper or zinc. It was also assumed that the ratio, r, found at 20°C would be the same at 25°C. The validity of these assumptions is considered below. These assumptions made it possible to evaluate the stepwise formation constants, k_4, of the tetrapyridine chlorides of manganese, cobalt, nickel, copper and zinc in chloroform at 25°C.

Next the ratio, s, of the stepwise formation constant, k_4, of cobalt tetrapyridine thiocyanate to that of cobalt tetrapyridine chloride, both in chloroform at 20°C was evaluated from the data of King et al. (98) and found to be 6.58×10^3. It was then assumed that this ratio did not vary much when the central metal (cobalt) was changed for manganese, nickel, copper or zinc. It was also assumed that the ratio, s, found at 20°C would be the same at 25°C. The validity of these assumptions is considered below. The values for r and s, and the assumptions related thereto, made it possible immediately to obtain from the data of Libus and Uruska (109), estimates of the stepwise formation constants of the tetrapyridine thiocyanates of manganese, cobalt, nickel, copper and zinc in chloroform at 25°C. These values are entered in column 4 of Table LXIII*.

It is necessary to consider whether or not the above assumptions concerning r and s are reasonable ones.

The ratio s is defined by equation (67):

$$s = \frac{{}^{CHCl_3}k_{4\,M_1P_4T_2}}{{}^{CHCl_3}k_{4\,M_1P_4Cl_2}} \qquad (67)$$

where ${}^{CHCl_3}k_{4\,M_1P_4T_2}$ and ${}^{CHCl_3}k_{4\,M_1P_4Cl_2}$ are, respectively, the stepwise formation constants of a metal tetrapyridine thiocyanate and a metal tetrapyridine chloride in chloroform at 20°C. The value of s was found to be 6.58×10^3 for the case where M_1 = cobalt.

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* In practice, the product rs was used for the calculation.

If

$$\left({}^{CHCl_3}\Delta H^{\circ}_{M_1P_4T_2} - {}^{CHCl_3}\Delta H^{\circ}_{M_1P_4Cl_2} \right) - \left({}^{CHCl_3}\Delta H^{\circ}_{M_2P_4T_2} - {}^{CHCl_3}\Delta H^{\circ}_{M_2P_4Cl_2} \right) =$$

$$T\left[\left({}^{CHCl_3}\Delta S^{\circ}_{M_1P_4T_2} - {}^{CHCl_3}\Delta S^{\circ}_{M_1P_4Cl_2} \right) - \left({}^{CHCl_3}\Delta S^{\circ}_{M_2P_4T_2} - {}^{CHCl_3}\Delta S^{\circ}_{M_2P_4Cl_2} \right) \right] \qquad (68)$$

then the value of s will be independent of the nature of the metal, M.

King, Koros and Nelson (98) found, for chloroform solutions, that the enthalpy change (ΔH°) for the configuration change $MP_2X_2 + 2P \rightleftharpoons MP_4X_2$ (M = cobalt; P = pyridine) did not vary much* for X = chloride, bromide, iodide, cyanate, thiocyanate and selenocyanate. Provided that a similar observation would be found for a metal other than cobalt, then the two bracketed terms on the left side of equation (68) are each nearly zero.

Libus and Uruska (109) stated that the entropy change (ΔS°) for the configuration change $MP_2Cl_2 + 2P = MP_4Cl_2$ (P = pyridine) would not change "significantly" for M = manganese, cobalt, nickel, copper and zinc. Provided that a similar observation would exist when chloroform rather than monochlorobenzene is the solvent, then

$$ {}^{CHCl_3}\Delta S^{\circ}_{M_1P_4Cl_2} = {}^{CHCl_3}\Delta S^{\circ}_{M_2P_4Cl_2} \qquad (69)$$

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* The values of ΔH° for these complexes were each the same, within $\pm$ 1.5 kcal mole^{-1}.

In addition, it may be expected that

$$ {}^{CHCl_3}\Delta S^{\circ}_{M_1P_4T_2} = {}^{CHCl_3}\Delta S^{\circ}_{M_2P_4T_2} \qquad (70) $$

when thiocyanate replaces chloride as the anion. It was concluded from the preceding discussion that the ratio s defined by equation (67) was, to a good approximation, independent of the central metal ion at 20°C. It was expected that the equalities described above would hold, within the errors of approximation, at 25°C, the temperature of the present investigation.

The ratio r is defined by equation (71):

$$ r = \frac{{}^{CHCl_3}k_{4_{M_1P_4Cl_2}}}{{}^{MCB}k_{4_{M_1P_4Cl_2}}} \qquad (71) $$

where ${}^{CHCl_3}k_{4_{M_1P_4Cl_2}}$ and ${}^{MCB}k_{4_{M_1P_4Cl_2}}$ are, respectively, the stepwise formation constants of a metal tetrapyridine chloride in chloroform and monochlorobenzene (MCB) solution. The value of r was found to be 1.46 for the case where M_1 = cobalt.

If

$$ {}^{CHCl_3}\Delta H^{\circ}_{M_2P_4Cl_2} - {}^{CHCl_3}\Delta H^{\circ}_{M_1P_4Cl_2} - T\left({}^{CHCl_3}\Delta S^{\circ}_{M_2P_4Cl_2} - {}^{CHCl_3}\Delta S^{\circ}_{M_1P_4Cl_2}\right) = \qquad (72) $$

$$ {}^{MCB}\Delta H^{\circ}_{M_2P_4Cl_2} - {}^{MCB}\Delta H^{\circ}_{M_1P_4Cl_2} - T\left({}^{MCB}\Delta S^{\circ}_{M_2P_4Cl_2} - {}^{MCB}\Delta S^{\circ}_{M_1P_4Cl_2}\right) $$

then the value of r will be independent of the nature of the metal, M.

Libus and Uruska (109) stated that

$$^{MCB}\Delta S^{\circ}_{M_1P_4Cl_2} = {}^{MCB}\Delta S^{\circ}_{M_2P_4Cl_2} \qquad (73)$$

From equations (69) and (73), equation (72) reduces to

$$^{CHCl_3}\Delta H^{\circ}_{M_2P_4Cl_2} - {}^{CHCl_3}\Delta H^{\circ}_{M_1P_4Cl_2} = {}^{MCB}\Delta H^{\circ}_{M_2P_4Cl_2} - {}^{MCB}\Delta H^{\circ}_{M_1P_4Cl_2} \qquad (74)$$

In order to discuss the validity of equation (74), consider the reaction

$$M_1P_2Cl_2 + 2P = M_1P_4Cl_2 \qquad (75)$$

in chloroform and in monochlorobenzene together with the reaction

$$M_1P_2Cl_{2(s)} + 2P_{(g)} = M_1P_4Cl_{2(s)} \qquad (76)$$

where the subscripts s and g indicate solid and gas phases, respectively. The symbols to be used in the argument are collected in Table LXIV.

From Hess' law

$$^{SOL}\Delta H^{\circ}_{M_1P_4Cl_2} = \Delta H^{\circ}_{1a} + 2\Delta H^{\circ}_{b} - \Delta H^{\circ}_{1c} + {}^{CHCl_3}\Delta H^{\circ}_{M_1P_4Cl_2}$$

$$= \Delta H^{\circ}_{1d} + 2\Delta H^{\circ}_{e} - \Delta H^{\circ}_{1f} + {}^{MCB}\Delta H^{\circ}_{M_1P_4Cl_2} \qquad (77)$$

from which

TABLE LXIV

Symbols used to describe heats of formation and heats of solution for the following reactions

$$M_1P_2Cl_2 + 2P = M_1P_4Cl_2$$
$$M_2P_2Cl_2 + 2P = M_2P_4Cl_2$$

$M_1P_2Cl_2 + 2P = M_1P_4Cl_2$					
Species	Heat of solution in:		Heat of formation in:		
	Chloroform	Monochlorobenzene	Solid phase	Chloroform	Monochlorobenzene
$M_1P_2Cl_{2(s)}$	ΔH°_{1a}	ΔH°_{1d}	-	-	-
$P_{(g)}$	ΔH°_{b}	ΔH°_{e}	-	-	-
$M_1P_4Cl_{2(s)}$	ΔH°_{1c}	ΔH°_{1f}	$_{SOL}\Delta H^\circ_{M_1P_4Cl_2}$	$_{CHCl_3}\Delta H^\circ_{M_1P_4Cl_2}$	$_{MCB}\Delta H^\circ_{M_1P_4Cl_2}$

NOTES: (1) For the reaction

$$M_2P_2Cl_2 + 2P = M_2P_4Cl_2$$

the above symbols also apply, except that the subscript 1 is replaced by 2.

(2) Subscripts s and g indicate solid and gas phases, respectively.

$$^{CHCl_3}\Delta H^{\circ}_{M_1P_4Cl_2} - {}^{MCB}\Delta H^{\circ}_{M_1P_4Cl_2} = \Delta H^{\circ}_{1d} + 2\Delta H^{\circ}_{e} - \Delta H^{\circ}_{1f} - \Delta H^{\circ}_{1a} - 2\Delta H^{\circ}_{b} + \Delta H^{\circ}_{1c} \qquad (78)$$

Similarly

$$^{CHCl_3}\Delta H^{\circ}_{M_2P_4Cl_2} - {}^{MCB}\Delta H^{\circ}_{M_2P_4Cl_2} = \Delta H^{\circ}_{2d} + 2\Delta H^{\circ}_{e} - \Delta H^{\circ}_{2f} - \Delta H^{\circ}_{2a} - 2\Delta H^{\circ}_{b} + \Delta H^{\circ}_{2c} \qquad (79)$$

By using equations (78) and (79), equation (74) may be written as follows:

$$(\Delta H^{\circ}_{1a} - \Delta H^{\circ}_{2a}) - (\Delta H^{\circ}_{1d} - \Delta H^{\circ}_{2d}) + (\Delta H^{\circ}_{1f} - \Delta H^{\circ}_{2f}) - (\Delta H^{\circ}_{1c} - \Delta H^{\circ}_{2c}) = 0 \qquad (80)$$

Nelson and Shepherd (113) have noted that the heats of solution of NiP_2I_2 and CoP_2I_2 (P = pyridine) in chloroform differ by only 0.4 kcal $mole^{-1}$. Provided that this observation would be found for the corresponding chloride complexes and for other metals, then

$$\Delta H^{\circ}_{1a} - \Delta H^{\circ}_{2a} \simeq 0 \qquad (81)$$

A similar observation would be expected if monochlorobenzene replaced chloroform as the solvent. Thus,

$$\Delta H^{\circ}_{1d} - \Delta H^{\circ}_{2d} \simeq 0 \qquad (82)$$

Nelson and Shepherd have shown (113) that the heats of

solution of solid cobalt and nickel tetrapyridine iodides in chloroform are, respectively, -3.24 and -2.40 kcal mole^{-1}. Provided that this observation would be found for the corresponding chloride complexes, and for other metals, then

$$\Delta H^{\circ}_{1c} - \Delta H^{\circ}_{2c} \simeq 0 \qquad (83)$$

A similar observation would be expected if monochlorobenzene replaced chloroform as solvent. Thus,

$$\Delta H^{\circ}_{1f} - \Delta H^{\circ}_{2f} \qquad (84)$$

From equations (81) to (84) it is seen that the equality expressed by equation (74) is very nearly true.

It was concluded from the preceding discussion that the ratio r defined by equation (71) was, to a good approximation, independent of the central metal ion at 20°C. It was expected that equalities described above would hold, within the errors of approximation, at 25°C, the temperature of the present investigation.

The computed values of k_4 in Table LXIII were therefore expected to approximate the true (but unreported, except for cobalt) values for the stepwise formation constants of those metal tetrapyridine thiocyanates in dried chloroform solution at 25°C.

The ratio, t, of the stepwise formation constant of cobalt tetrapyridine thiocyanate in benzene to that in chloroform at 25°C was known (119) to be 3.9. It was considered reasonably safe to assume

that this ratio did not vary much when the central metal (cobalt) was changed for manganese, nickel, copper or zinc. This assumption may be supported by an argument similar to that given above for the ratio r. It made possible the estimation of the stepwise formation constants of the tetrapyridine thiocyanates of manganese, cobalt, nickel, copper and zinc in benzene at 25°C. These values are also included in Table LXIII.

Nelson and Shepherd (113) have reported the stepwise formation constants of nickel tetra-3-picoline and tetrapyridine iodides in dried chloroform at 20°C. Their ratio*, v, could therefore be calculated; the value found was v = 0.307. It was assumed that this ratio did not vary much either when the central metal (nickel) was changed for manganese, cobalt, copper or zinc, or when thiocyanate replaced iodide as ligand. It was also assumed that the ratio at 25°C would be the same as it was at 20°C. The validity of these assumptions is considered below. The assumptions made it possible to estimate the stepwise formation constants of the tetra-3-picoline thiocyanates of manganese, cobalt, nickel, copper and zinc in chloroform at 25°C. These values are in column 4 of Table LXIII.

It is necessary to justify the assumptions. The ratio v is defined by equation (85):

$$v = \frac{CHCl_3 k_4 M_1 (3\text{-}P)_4 I_2}{CHCl_3 k_4 M_1 P_4 I_2} \qquad (85)$$

* The constant for the pyridinate was in the denominator.

where ${}^{CHCl_3}k_{4_{M_1(3\text{-}P)_4I_2}}$ and ${}^{CHCl_3}k_{4_{M_1P_4I_2}}$ are, respectively, the stepwise formation constants of a metal tetra-3-picoline iodide and a metal tetrapyridine iodide in chloroform. The value of v was found to be 0.307 for the case where M_1 = nickel.

If

$$\left({}^{CHCl_3}\Delta H^{\circ}_{M_1(3\text{-}P)_4I_2} - {}^{CHCl_3}\Delta H^{\circ}_{M_1P_4I_2}\right) - \left({}^{CHCl_3}\Delta H^{\circ}_{M_2(3\text{-}P)_4I_2} - {}^{CHCl_3}\Delta H^{\circ}_{M_2P_4I_2}\right) = \tag{86}$$

$$T\left[\left({}^{CHCl_3}\Delta S^{\circ}_{M_1(3\text{-}P)_4I_2} - {}^{CHCl_3}\Delta S^{\circ}_{M_2(3\text{-}P)_4I_2}\right) - \left({}^{CHCl_3}\Delta S^{\circ}_{M_1P_4I_2} - {}^{CHCl_3}\Delta S^{\circ}_{M_2P_4I_2}\right)\right]$$

then the value of v will be independent of the nature of the metal, M.

Arguments similar to those presented above indicate that the two bracketed terms on the right side of equation (86) should each be nearly zero.

Nelson and Shepherd (113) found for chloroform solutions that ΔH° for the configuration change $NiP_2I_2 + 2P = NiP_4I_2$ did not vary much* for P = pyridine or P = 3-picoline. Provided that a similar statement can be made for a metal other than nickel, then the two bracketed terms on the left side of equation (86) would each be approximately zero.

By using the foregoing assumptions it is seen that the ratio v, defined by equation (85) would be independent of the metal ion.

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* The values of ΔH° for these complexes were each the same, within $\pm$ 1 kcal mole^{-1}.

It was also assumed* that the ratio v was the same for the case where thiocyanate replaced iodide as the anion in the complex. It was expected that the ratio v would hold, within the errors of approximation, at 25°C, the temperature of the present investigation.

Finally, Nelson and Shepherd (97) have implied that the stepwise formation constants of nickel tetrapyridine thiocyanate and nickel tetra-4-picoline thiocyanate are approximately equal. This relationship was assumed to be valid for the metals manganese, cobalt, copper and zinc so that estimates could be obtained for the stepwise formation constants of the metal tetra-4-picoline thiocyanates. The values are in column 4 of Table LXIII.

King, Koros and Nelson (98) have estimated the stepwise formation constant of cobalt tetra-2-picoline thiocyanate in chloroform at 20°C to be approximately 10^{-6}. This value was entered in column 4 of Table LXIII.

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* This assumption may be supported by an argument similar to that shown above for the ratio s, and by using the observation of King, Koros and Nelson (98) that, for a given metal, ΔH is approximately independent of the anion in the complex.

2-1. Effect of the Pyridine and Picoline Ligands

Nelson and Shepherd (113) found that the stepwise formation constant (in chloroform) for nickel tetrapyridine iodide is about three times larger than that for nickel tetra-3-picoline iodide; they also suggested (97) that the stepwise formation constants (in chloroform) of nickel tetrapyridine thiocyanate and nickel tetra-4-picoline thiocyanate in chloroform are approximately equal.

Nelson and Shepherd (97) explain these results on the basis of pyridine, 3-picoline and 4-picoline having different charge densities and charge distributions on their rings: "Since the methyl substituent directs charge into the ring inductively, it might be expected that both 3-picoline and 4-picoline should be less efficient pi-electron acceptors than pyridine. Moreover, in 4-picoline the mesomeric effect is such that the 1-, 3- and 5-positions are those of greatest electron density and the 2-, 4- and 6-positions those of least electron density. The converse is true of 3-picoline. Similarly, back-coordinated charge from the metal to the pyridine ring will be localized mainly on the 2-, 4- and 6-positions. These are the same positions that in 3-picoline already carry an excess of charge, so in complexes with this amine back-donation should be inhibited in comparison with 4-picoline complexes .... . Thus, the pi-acceptor capacity should be pyridine > 4-picoline > 3-picoline. However, 4-picoline ($pK_a = 6.02$) is a stronger base at 25°C than pyridine ($pK_a = 5.17$) and it is not unlikely that the greater availability of the sigma-bonding electrons in 4-picoline compensates for the smaller pi-contribution."

Desai and Kabadi (115) noted for an aqueous system that the

presence of an alkyl group on the pyridine ring increased the availability of electrons on the nitrogen atom. They demonstrated that there is a linear relationship between the negative logarithm of the acid dissociation constant*, pK_a, and the logarithm of the first stepwise formation constant in aqueous solution for the pyridine, 3-picoline and 4-picoline complexes** of zinc (114) and cadmium (115). They did not use the overall formation constant; however, an examination of their data showed that pK_a is approximately a linear function of log K_i, where K_i is the overall formation constant of the i^{th} metal pyridine (or picoline) complex ion.

These results of Nelson and Shepherd and of Desai and Kabadi will be used later in discussing the results of the present investigation.

The partition coefficients of the ligands themselves between chloroform and 0.3-M potassium thiocyanate solution are in the order pyridine (14.1) < 2-picoline (41.2) < 4-picoline (47.2) < 3-picoline (54.7) as shown in Table LXIII. Other investigators (116) found the following order: pyridine (27) < 2-picoline (62) < 3-Picoline (75) < 4-picoline (77). Their partition coefficients, p, were calculated from the equation

$$\log p' = pH + \log p - pK_a$$

by using literature values of pK_a and the apparent partition coefficients***,

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* K_a is the equilibrium constant for the reaction $PH^+ = P + H^+$.

** Zinc and cadmium formed complex ions of the type MP_m (P = pyridine, 3-picoline or 4-picoline; m = 1, 2, 3).

*** The apparent partition coefficient, p', is defined as the total pyridine (or picoline) concentration in the chloroform phase divided by the total pyridine (or picoline) concentration in the aqueous phase (pyridine plus pyridinium, or picoline plus picolinium).

p', of pyridine and the picolines between chloroform and an aqueous citrate-phosphate buffer solution at pH 4.00. By using the more recent literature values for pK_a given in Table LXV, the following partition coefficients were calculated: pyridine, 12.9; 2-picoline, 51.3; 3-picoline, 58.8; 4-picoline, 55.0, an order which agrees with that found in the present investigation. It was concluded that the partition coefficients, p, found in the present investigation were more reliable than those reported values (116) since the latter depended upon a calculation involving the use of a constant, pK_a, which is not known precisely.

The partition coefficients of pyridine and the picolines between chloroform and 0.3-M potassium thiocyanate solution together with their pK_a values are in Table LXV. The argument of Nelson and Shepherd (97) quoted above can be applied successfully to explain the order of the pK_a values. In seeking a relationship between the partition coefficients and the pK_a values it must be remembered that the partition coefficient depends not only on the pK_a value but also on the size of the molecule. Collander (117) has shown that the partition coefficient increases between two- and four-fold for every additional methylene group incorporated in the molecule. Consequently, it is reasonable to suppose that the addition of a methyl group to the pyridine ring will increase the partition coefficient by a factor of about three. The measured partition coefficients are in fact of about the correct order of magnitude with pyridine being less by a factor of between three and four than the picolines. In order to explain the order of the picoline partition coefficients (2-picoline < 4-picoline < 3-picoline) the

TABLE LXV

Partition coefficients and pK_a values for pyridine bases at 25°C

Pyridine base	pK_a	Partition coefficient
Pyridine	5.17	14.1
2-Picoline	5.97	41.2
3-Picoline	5.68	54.7
4-Picoline	6.02	47.2
2-Ethylpyridine	5.97	-
3-Ethylpyridine	5.70	-
4-Ethylpyridine	6.02	-
2-Isopropylpyridine	5.83	-
3-Isopropylpyridine	5.72	-
4-Isopropylpyridine	6.02	-
2-t-Butylpyridine	5.76	-
3-t-Butylpyridine	5.82	-
4-t-Butylpyridine	5.99	-
2-n-Propylpyridine	5.97	-
2,6-Dimethylpyridine	6.75	-

NOTES: (1) The partition coefficients are those between chloroform and 0.3-M potassium thiocyanate solution.

(2) $K_a = \frac{[P][H]}{[PH]}$; $pK_a = -\log K_a$.

(3) pK_a data are from reference (22).

(4) Partition coefficients are from Table LXIII.

following, although admittedly tenuous explanation is offered: it is supposed that the interaction between the nitrogen of the picoline and water is greater in all cases, than that between the nitrogen of the picoline and chloroform. The argument of Nelson and Shepherd (97) quoted above shows that this interaction, in the case of 3-picoline, will be less than that for either 2- or 4-picoline; consequently, 3-picoline will be the most readily extracted picoline. If it is also assumed that the effective molecular volume of 2-picoline is less than that of 4-picoline, then more energy is gained when the hole in the aqueous phase collapses on extraction of 4-picoline; consequently 4-picoline would be more readily extracted than 2-picoline.

The values of $p_2 K_{2,2}$ and $p_4 K_{4,2}$ listed in Table LXIII were, for each metal, divided by the value found for the metal pyridine thiocyanate*. These values, listed in Table LXVI may be more readily compared. It is seen from these relative values that for a given metal, the order of $p_2 K_{2,2}$ and $p_4 K_{4,2}$ is pyridine $<<$ 3-picoline $<$ 4-picoline.

By using the bond lengths and atomic radii of Pauling (123), estimates were obtained for the molecular volumes of the metal pyridine and picoline thiocyanates.

The thiocyanate molecule was taken to have a length** of 3.82 Å. For a pyridine molecule, the distance from the centre of the nitrogen atom to the outermost hydrogen atom at the 4-position was taken to be

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* The values obtained for cobalt 2-picoline thiocyanate and for the benzene extraction of nickel pyridine thiocyanate were not considered.

** This length was obtained by adding the atomic radius of sulphur (1.04 Å) to the sum of the reported bond lengths (N-C, 1.22 Å; C-S, 1.56 Å).

TABLE LXVI

Relative values of $p_2 K_2$ and $p_4 K_4$ for the metal pyridine and picoline thiocyanates

Metal (II)	Ligand	$p_2 K_{2,2}$	$p_4 K_{4,2}$
Cobalt	Pyridine	1	1
	3-Picoline	61	289
	4-Picoline	143	1600
Nickel	Pyridine	1	1
	3-Picoline	58	260
	4-Picoline	151	1700
Zinc	Pyridine	1	1
	3-Picoline	98	438
	4-Picoline	166	1880
Cadmium	Pyridine	-	1
	3-Picoline	-	533
	4-Picoline	-	1790

NOTES: (1) The values were obtained by dividing each value of $p_2 K_{2,2}$ (or $p_4 K_{4,2}$), for a given metal, by the value found when pyridine was the ligand.

(2) Basic data are from Table LXIII.

3.75 A. For a 4-picoline molecule, the distance from the centre of the nitrogen atom to the outermost hydrogen atom of the methyl group was taken to be 5.28 A. In addition, Pauling (123) has listed the atomic radii of the metals. A comparison of his values for tetrahedral covalent radii, octahedral covalent radii, single bond radii, and for the effective radii of metals in diatomic hydride molecules showed that a maximum error of about $\pm$ 0.08 Å would result from assuming that the single bond metal radii represented the effective metal radii in either tetrahedral or octahedral geometries, the configurations of the metal pyridine and picoline thiocyanates.

From these metal radii, together with the lengths of the thiocyanate, pyridine and 4-picoline molecules, the molecular volume, V, was estimated for each of the metal pyridine and 4-picoline thiocyanates. The following equation was used:

$$V = \pi \left(r_M + \frac{m l_P + n l_T}{m + n} \right)^3$$

where l_P and l_T are the lengths of the pyridine (or 4-picoline) and thiocyanate molecules, respectively, and m and n are the numbers of pyridine (or 4-picoline) and thiocyanate molecules, respectively, bound to the central metal ion of radius r_M. Each value of V then was multiplied by the factor $\frac{m}{m + n}$ to give an estimate of the "effective" molecular volume*, V_E, of the particular complex in solution. These

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* It is expected that solvent molecules could be accommodated to some extent in the interstitial space between the ligands of either a tetrahedral metal dipyridine (or dipicoline) thiocyanate or an octahedral metal tetrapyridine (or tetrapicoline) thiocyanate. Thus, the "effective" molecular volume of each complex would be less than the molecular volume V. The effective molecular volume of a tetrahedral complex would be expected to comprise a smaller proportion of V than the corresponding octahedral complex since the interstitial space between the ligands would be greater for the tetrahedral complex.

estimates* of the effective molecular volumes are in Table LXVII.

From these estimates for the metal pyridine and 4-picoline thiocyanate complexes, it is seen that, for a given metal in either a tetrahedral or an octahedral configuration, the 4-picolinate has a larger effective molecular volume than the corresponding pyridinate. Moreover, for a given metal, the tetrapyridine (or tetra-4-picoline) thiocyanate has a larger effective molecular volume than the corresponding dipyridine (or di-4-picoline) thiocyanate. Those complexes with the larger effective molecular volumes would be expected to have larger partition coefficients since the energy gained when the hole in the aqueous phase of the extraction system collapses will also be larger. Moreover it is expected that the 4-picolinates would have slightly larger partition coefficients than the corresponding 3-picolinates; the methyl substituents of the 4-picolinates point directly away from the central metal ion and probably produce a greater effective molecular volume than the 3-picolinates, where the positional groups are tucked into the side of the metal complex.

It is also seen from the data in Table LXVII that the effective molecular volume of a given complex is approximately independent of the central metal ion. Thus it is expected that the partition coefficient, p_2, of each metal dipyridine thiocyanate would have approximately the same value. Similarly, the partition coefficient, p_4, of each metal tetrapyridine thiocyanate would be expected to have approximately the same value. Analogous effects would be expected if a picoline were substituted for pyridine.

It was concluded from the preceding discussion that (i) for a

* It is not implied that the estimates are quantitative.

TABLE LXVII

Estimates of the effective molecular volumes, V_E, for the metal dipyridine and di-4-picoline thiocyanates (MP_2T_2), and for the metal tetrapyridine and tetra-4-picoline thiocyanates (MP_4T_2)

Metal (II)	Ligand	V_E, $(Å)^3$	
		MP_2T_2	MP_4T_2
Cobalt	Pyridine	190	251
	4-Picoline	292	442
Nickel	Pyridine	189	249
	4-Picoline	290	441
Zinc	Pyridine	201	265
	4-Picoline	306	463
Cadmium	Pyridine	221	291
	4-Picoline	332	501

NOTE: The effective molecular volumes were calculated from the equation:

$$V_E = \frac{4}{3}\pi\left(r_M + \frac{ml_P + nl_T}{m+n}\right)^3 \cdot \frac{m}{m+n}$$

where: l_P = length of a pyridine molecule (3.75 Å) or a 4-picoline molecule (5.28 Å).
l_T = length of a thiocyanate molecule (3.82 Å)
m = number of pyridine (or picoline) ligands in the complex.
n = number of thiocyanate ligands in the complex.
r_M = radius of central metal ion. The following values were used:

cobalt, 1.16 Å; nickel, 1.15 Å; zinc, 1.25 Å; cadmium, 1.41 Å.

given pyridine or picoline ligand, the partition coefficient (p_2 or p_4) would be approximately independent of the central metal ion; and (ii) for a given metal, the partition coefficient (p_2 or p_4) would increase in the ligand order pyridine < 3-picoline < 4-picoline.

This ligand order for p_2 or p_4 (pyridine < 3-picoline < 4-picoline) is the same order as that found for both $p_2 K_{2,2}$ and $p_4 K_{4,2}$ for each of the metals cobalt, nickel, zinc and cadmium.

The formation constants of the extractable metal pyridine and picoline thiocyanates in aqueous solution have not been reported in the literature, and their magnitude is unknown. However, the results of Desai and Kabadi (114,115) noted above suggest that the ligand order for the overall formation constant $K_{2,2}$ (or $K_{4,2}$) of a given metal would be pyridine < 3-picoline < 4-picoline. This order agrees with the ligand order found for $p_2 K_{2,2}$ and $p_4 K_{4,2}$ for each of the metals studied in the present investigation.

It is worth noting that the ligand order found by Nelson and Shepherd (97,113) for the stepwise formation constants of nickel tetrapyridine and tetrapicoline iodides in chloroform solution is 3-picoline < pyridine = 4-picoline; this is also the ligand order for the stepwise formation constants of the metal tetrapyridine and tetrapicoline thiocyanates in chloroform solution (see Table LXIII). The relationship between the stepwise formation constant of a metal tetrapyridine or tetrapicoline thiocyanate in aqueous solution ($K_{4,2} \cdot K_{2,2}^{-1}$) and that in non-aqueous solution is given by

$$\frac{K_{4,2}}{K_{2,2}} = k_4 p^2 \frac{p_2}{p_4} \qquad (64)$$

Provided that the ratio $\frac{p_2}{p_4}$ remains approximately constant when a picoline is substituted for pyridine, then by using the tabulated values of k_4 and p, it is evident that the ligand order for the stepwise formation constants of the tetrapyridine and tetrapicoline thiocyanates of a given metal in aqueous solution ($K_{4,2}.K_{2,2}^{-1}$) is also pyridine < 3-picoline < 4-picoline.

It was therefore concluded for a given metal that the ligand order for p_2, p_4, $K_{2,2}$ and $K_{4,2}$ would be pyridine < 3-picoline < 4-picoline. Thus a reasonable explanation had been found for the ligand orders of $p_2 K_{2,2}$ and $p_4 K_{4,2}$ for a given metal.

2-2. Effect of the Central Metal Ion

The values of $p_4 K_{4,2}$ and $p_2 K_{2,2}$ were known for (i) the chloroform extraction of the pyridine, 3-picoline and 4-picoline thiocyanates of cobalt, nickel and zinc; (ii) the chloroform extraction of cobalt 2-picoline thiocyanate; and (iii) the benzene extraction of nickel pyridine thiocyanate. The value of k_4, the stepwise formation constant in the organic phase was also known for these complexes as well as for the pyridine, 3-picoline and 4-picoline thiocyanates of manganese and copper*. These data are in Table LXIII. For purposes of interpretation, it was considered useful to estimate the values of $p_2 K_{2,2}$ and/or $p_4 K_{4,2}$ for (i) the chloroform extraction of the pyridine, 3-picoline and 4-picoline thiocyanates of manganese, iron and copper; (ii) the chloroform extraction of the 2-picoline thiocyanates of manganese, iron, nickel, copper and zinc; and (iii) the benzene extraction of the

* Only the values of $p_4 K_{4,2}$ were known for the pyridine, 3-picoline and 4-picoline thiocyanates of cadmium.

pyridine thiocyanates of manganese, iron, cobalt, copper and zinc. The method used to obtain these estimates is described below.

The known values of log $p_4 K_{4,2}$, log k_4 and* log k_4' were plotted against the atomic number of the central metal ion. These plots are in Fig. 52. Curves A, B and C were seen to be almost identical in shape, and to be quite similar in shape to curves E and G which were also seen to be almost identical in shape. This similarity suggested that, by drawing the branches of curves A, B and C from cobalt to manganese parallel to those corresponding branches in curves E and G, estimates could be obtained of $p_4 K_{4,2}$ for the pyridine, 3-picoline and 4-picoline thiocyanates of manganese and iron; the corresponding estimates of $p_4 K_{4,2}$ for copper were obtained by interpolation.

Only one value of $p_4 K_{4,2}$ was available for the 2-picoline thiocyanate system. In order to obtain estimates of $p_4 K_{4,2}$ for the other metal 2-picoline thiocyanates, a curve parallel to curve C was drawn through the known value of $p_4 K_{4,2}$ for cobalt 2-picoline thiocyanate. These estimates are likely to be only of semi-quantitative use since it was shown in Part VII-1 that steric hindrance was very severe in these complexes; the degree of steric hindrance is likely to be sensitive to small differences in the atomic radii of these metals. This sensitivity would probably be reflected in the magnitude of the overall formation constant, $K_{4,2}$, and hence in $p_4 K_{4,2}$.

Only one value of $p_4 K_{4,2}$ was available for the case where

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* The values of log k_4' are the literature values (109) for the stepwise formation constants, in monochlorobenzene at 25°C, of the pyridine chlorides of manganese, cobalt, nickel, copper and zinc.

FIGURE 52

Log $p_4 K_{4,2}$, log k_4 and log k_4' versus the atomic number of the central metal ion; temperature, 25°C.

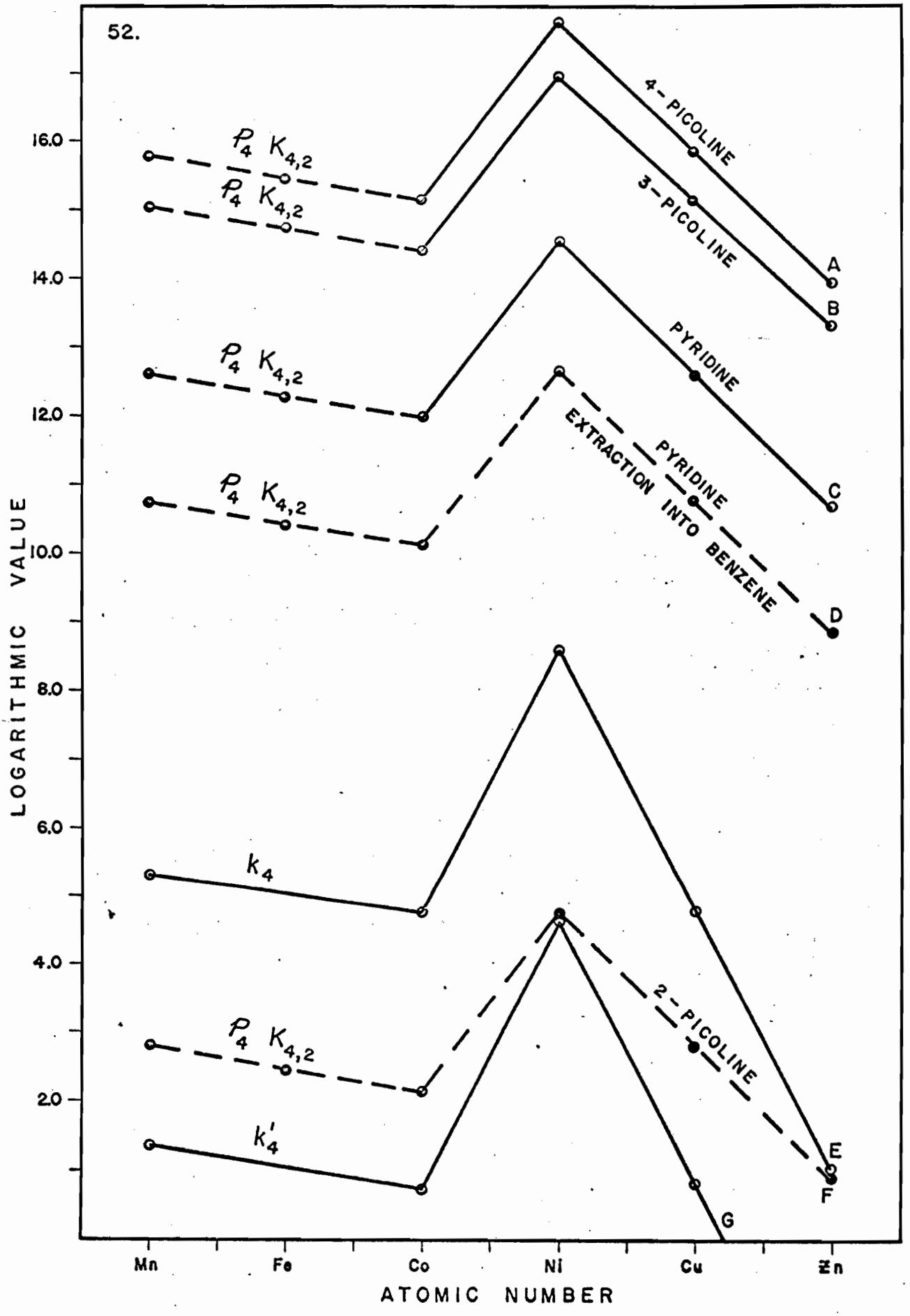
NOTES: (1) p_4 is the partition coefficient, between chloroform (or benzene) and 0.3-M potassium thiocyanate solution, of a metal tetrapyridine or tetrapicoline thiocyanate.

(2) $K_{4,2}$ is the overall formation constant of a metal tetrapyridine or tetrapicoline thiocyanate in aqueous solution.

(3) k_4 is the stepwise formation constant of a metal tetrapyridine thiocyanate in chloroform solution.

(4) k_4' is the stepwise formation constant of a metal tetrapyridine chloride in monochlorobenzene solution.

(5) Data for $p_4 K_{4,2}$ and k_4 from Table LXIII are indicated by open circles, as are the literature data (109) for k_4'; extrapolated or interpolated values of $p_4 K_{4,2}$ are indicated by closed circles.


52.
4-PICOLINE
3-PICOLINE
PYRIDINE
PYRIDINE
EXTRACTION INTO BENZENE
2-PICOLINE
A
B
C
D
E
F
G
$P_4\ K_{4,2}$
$P_4\ K_{4,2}$
$P_4\ K_{4,2}$
$P_4\ K_{4,2}$
$P_4\ K_{4,2}$
k_4
k'_4
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
LOGARITHMIC VALUE
Mn
Fe
Co
Ni
Cu
Zn
ATOMIC NUMBER

benzene was used as the solvent. In order to obtain estimates of $p_4 K_{4,2}$ for the benzene extraction of the other metal pyridine thiocyanates, a curve parallel to curve C was drawn through the known value of $p_4 K_{4,2}$ for nickel pyridine thiocyanate.

The estimates and the experimental values of $p_4 K_{4,2}$, $p_2 K_{2,2}$ and k_4 are given together in Table LXVIII. It is emphasized that the estimates obtained above by either extrapolation or interpolation are speculative in nature. However, it will be shown below that from them useful predictions may be made about future experiments.

The relationship between $p_4 K_{4,2}$, $p_2 K_{2,2}$ and k_4 is given by

$$k_4 = \frac{p_4 K_{4,2}}{p_2 K_{2,2}} \cdot \frac{1}{p^2} \qquad (64)$$

where p is the partition coefficient of free pyridine (or picoline) between the two phases of the specified solvent-extraction system. By using the tabulated values of $p_4 K_{4,2}$, together with the values of k_4 and p, it was thus possible to calculate the values of $p_2 K_2$ for (i) the chloroform extraction of the pyridine, 3-picoline and 4-picoline thiocyanates of manganese and copper; and (ii) the benzene extraction of the pyridine thiocyanates of manganese, cobalt, copper and zinc. These values are given in column 6 of Table LXVIII.

The values of $p_2 K_{2,2}$ calculated for the benzene extraction of the pyridine thiocyanates of manganese, cobalt, nickel, copper and zinc were plotted against the atomic number of the central metal ion. Similarly, the values of $p_2 K_{2,2}$ for the chloroform extraction of the pyridine, 3-picoline and 4-picoline thiocyanates of manganese, cobalt,

TABLE LXVIII

Values of k_4, $p_2 K_{2,2}$ and $p_4 K_{4,2}$ for the metal pyridine and picoline thiocyanates at 25°C

Metal (II)	Ligand	p	k_4	log k_4	$p_2 K_{2,2}$	log $p_2 K_{2,2}$	$p_4 K_{4,2}$	log $p_4 K_{4,2}$
Manganese	Pyridine	14.1	2.3×10^{5}	5.36	(8.5×10^{4})	(4.93)	(3.9×10^{12})	(12.59)
	Pyridine*	2.93	9.0×10^{5}	5.95	(7.2×10^{3})	(3.86)	(5.5×10^{10})	(10.74)
	2-Picoline	41.2	-	-	-	-	(6.0×10^{2})	(2.78)
	3-Picoline	54.7	7.1×10^{4}	4.85	(5.2×10^{6})	(6.72)	(1.1×10^{15})	(15.05)
	4-Picoline	47.2	2.3×10^{5}	5.36	(1.2×10^{7})	(7.09)	(6.2×10^{15})	(15.79)
Iron	Pyridine	14.1	(1.1×10^{5})	(5.05)	(8.5×10^{4})	(4.93)	(1.0×10^{12})	(12.28)
	Pyridine*	2.93	(4.4×10^{5})	(5.64)	(7.2×10^{3})	(3.86)	(2.7×10^{10})	(10.43)
	2-Picoline	41.2	-	-	-	-	(1.8×10^{2})	(2.47)
	3-Picoline	54.7	(3.4×10^{4})	(4.54)	(5.2×10^{6})	(6.72)	(5.5×10^{14})	(14.74)
	4-Picoline	47.2	(1.1×10^{5})	(5.05)	(1.2×10^{7})	(7.09)	(3.0×10^{15})	(15.48)
Cobalt	Pyridine	14.1	5.4×10^{4}	4.73	8.4×10^{4}	4.92	9.02×10^{11}	11:96
	Pyridine*	2.93	2.1×10^{5}	5.32	(7.2×10^{3})	(3.86)	(1.3×10^{10})	(10.11)
	2-Picoline	41.2	10^{-6}	6.00	8.51×10^{4}	4.93	1.4×10^{2}	2.15
	3-Picoline	54.7	1.7×10^{4}	4.23	5.1×10^{6}	6.71	2.61×10^{14}	14.42
	4-Picoline	47.2	5.4×10^{4}	4.73	1.2×10^{7}	7.08	1.44×10^{15}	15.16

(continued)

TABLE LXVIII (continued)

Metal (II)	Ligand	p	k_4	log k_4	$p_2 K_{2,2}$	log $p_2 K_{2,2}$	$p_4 K_{4,2}$	log $p_4 K_{4,2}$
	Pyridine	14.1	4.0×10^8	8.60	4.3×10^3	3.63	3.42×10^{14}	14.53
	Pyridine*	2.93	1.6×10^9	9.19	3.5×10^2	2.54	4.77×10^{12}	12.68
Nickel	2-Picoline	41.2	-	-	-	-	$(5.2 \times 10^4$	(4.72)
	3-Picoline	54.7	1.2×10^8	8.08	2.5×10^5	5.40	8.87×10^{16}	16.95
	4-Picoline	47.2	4.0×10^8	8.60	6.5×10^5	5.81	5.83×10^{17}	17.77
	Pyridine	14.1	6.5×10^4	4.81	(3.2×10^5)	(5.50)	(4.0×10^{12})	(12.60)
	Pyridine*	2.93	2.5×10^4	5.40	(2.7×10^4)	(4.43)	(5.8×10^{10})	(10.76)
Copper	2-Picoline	41.2	-	-	-	-	(6.3×10^2)	2.80
	3-Picoline	54.7	2.0×10^4	4.30	(1.8×10^7)	(7.25)	(1.4×10^{15})	(15.14)
	4-Picoline	47.2	6.5×10^4	4.81	(5.0×10^7)	(7.70)	(7.2×10^{15})	(15.86)
	Pyridine	14.1	10	1.00	2.43×10^7	7.39	4.8×10^{10}	10.68
	Pyridine*	2.93	39	1.59	(2.0×10^6)	(6.31)	(6.8×10^8)	(8.83)
Zinc	2-Picoline	41.2	-	-	-	-	(7.4)	(0.87)
	3-Picoline	54.7	3	0.48	2.38×10^9	9.38	2.1×10^{13}	13.32
	4-Picoline	47.2	10	1.00	4.02×10^9	9.60	9.0×10^{13}	13.95

(continued)

TABLE LXVIII (continued)

Metal (II)	Ligand	p	k_4	log k_4	$p_2 K_{2,2}$	log $p_2 K_{2,2}$	$p_4 K_{4,2}$	log $p_4 K_{4,2}$
	Pyridine	14.1	-	-	-	-	2.76×10^{11}	11.44
	Pyridine*	2.93	-	-	-	-	-	-
Cadmium	2-Picoline	41.2	-	-	-	-	-	-
	3-Picoline	54.7	-	-	-	-	1.47×10^{14}	14.17
	4-Picoline	47.2	-	-	-	-	4.95×10^{14}	14.69

* Extraction into benzene.

NOTES: (1) Brackets denote values of k_4, $p_4 K_{4,2}$ and $p_2 K_{2,2}$ found from

$$k_4 = \frac{p_4 K_{4,2}}{p_2 K_{2,2}} \frac{1}{p^2} \qquad (64)$$

by using extrapolated or interpolated values of $p_4 K_{4,2}$ and/or $p_2 K_{2,2}$; all other values were taken from Table LXIII.

(2) For definitions of k_4, p_2, p_4, $K_{2,2}$ and $K_{4,2}$, see equations (64) to (66).

(3) p is the partition coefficient of pyridine or a picoline.

nickel, copper and zinc were plotted against the atomic number of the central metal ion. These plots (not shown) allowed the value of $p_2 K_{2,2}$ to be interpolated for the benzene extraction of iron pyridine thiocyanate and for the chloroform extraction of iron pyridine, 3-picoline and 4-picoline thiocyanates.

By using the estimates given in Table LXVIII of $p_2 K_{2,2}$ and $p_4 K_{4,2}$ for the extraction of (i) iron pyridine thiocyanate into benzene; and (ii) iron pyridine, 3-picoline and 4-picoline thiocyanates into chloroform it was possible to calculate from equation (64) the corresponding values of the stepwise formation constants, k_4, for these complexes in non-aqueous solution. These values are also included in Table LXVIII.

From the data in Table LXVIII, certain trends in the data relating to the effect of the central metal ion were evident. These trends are summarized in Table LXIX; they were the same for pyridine, 2-picoline, 3-picoline and 4-picoline*. The calculation of the effective molecular volumes of the complexes, described previously, suggested that it was not unreasonable to suppose that the partition coefficients p_2 and p_4 are influenced principally by the pyridine or picoline ligand, and to a minor degree by the central metal ion. Although conclusive evidence for this supposition was not presented, it will now be used as a working hypothesis. Thus, in Table LXIX, the order of the metals for $p_4 K_{4,2}$ is also the order for $K_{4,2}$, the overall formation constant of a metal tetrapyridine or tetrapicoline thiocyanate in aqueous solution.

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* The values of $p_2 K_{2,2}$ for manganese, iron and cobalt are equivalent; this is due to the nature of the extrapolation procedure used to obtain $p_2 K_{2,2}$.

TABLE LXIX

Trends in the stability constants of some metal complexes

Complex	Trend
Metal pyridine, 3-picoline and 4-picoline thiocyanates; extraction into chloroform	$p_4 K_{4,2}$: Zn<Cd<Co<Fe<Mn<Cu<Ni $p_2 K_{2,2}$: Ni<Mn=Fe=Co<Cu<Zn k_4 : Zn<Co<Cu<Fe<Mn<Ni
Metal 2-picoline thiocyanates; extraction into chloroform	$p_4 K_{4,2}$: Zn<Co<Fe<Mn<Cu<Ni
Metal pyridine thiocyanates; extraction into benzene	$p_4 K_{4,2}$: Zn<Co<Fe<Mn<Cu<Ni $p_2 K_{2,2}$: Ni<Mn=Fe=Co<Cu<Zn k_4 : Zn<Co<Cu<Fe<Mn<Ni
Many metal-ligand complexes; aqueous solution*	Overall or stepwise formation constant: Mn<Fe<Co<Ni<Cu>Zn
Metal pyridine chlorides; monochlorobenzene solution**	k_4' : Zn<Co<Cu<Mn<Ni

* Irving and Williams (66)

** Libus and Uruska (109)

NOTES: (1) For definitions of k_4, p_2, p_4, $K_{2,2}$ and $K_{4,2}$, see equations (64) to (66).

(2) $$k_4' = \frac{[MP_4Cl_2]_o}{[MP_2Cl_2]_o [P]_o^2} \; ; \quad P = \text{Pyridine}$$

Similarly, the order of the metals for $p_2 K_{2,2}$ is also the order for $K_{2,2}$, the overall formation constant of a metal dipyridine or dipicoline thiocyanate in aqueous solution.

Irving and Williams (66) found the following stability order for many ligands in aqueous solution: manganese < iron < cobalt < nickel < copper > zinc; they pointed out that this was also the order for the second ionization potentials of these metals.

A comparison of the Irving-Williams order with that for $p_2 K_{2,2}$ shows that the orders are in general agreement, except for nickel. This agreement lends support to the hypothesis that the partition coefficient p_2 depends mainly upon the pyridine or picoline ligand, and not upon the metal.

Libus and Uruska (109) have measured the stepwise formation constants of some metal tetrapyridine chlorides in monochlorobenzene solution; the order of stability of the transition metals they studied is also in Table LXIX. This order, as well as the order for k_4, the stepwise formation constant of a metal tetrapyridine or tetrapicoline thiocyanate in chloroform solution, may be compared with the order for $p_4 K_{4,2}$ and seen to be in general agreement, except for copper*.

If it is assumed that the ratio $\frac{p_2}{p_4}$ is approximately independent of the central metal ion, then it is seen from equation (64)

$$\frac{K_{4,2}}{K_{2,2}} = k_4 p^2 \frac{p_2}{p_4} \qquad (64)$$

* The anomalous position of copper in the order for $p_4 K_{4,2}$ was not considered significant in view of the fact that the values of $p_4 K_{4,2}$ for copper, iron and manganese were all nearly the same (see Table LXVIII), and all were obtained either by extrapolation or interpolation.

that the order for the stepwise formation constants of metal tetrapyridine (or tetrapicoline) thiocyanates in either aqueous or non-aqueous solution must be identical. This order is zinc < cobalt < copper < iron < manganese < nickel; it represents the relative tendency of a metal to form an (extractable) metal tetrapyridine (or tetrapicoline) thiocyanate.

Nelson and Shepherd (113) have shown that there is an increasing stability of the tetrahedral state on passing from manganese to zinc. In addition, it has been shown (109) that crystal field stabilization effects, superimposed on a continuous decrease of the relative stability of octahedral complexes between manganese and zinc, allow for a qualitative explanation of the differences between individual metal ions with respect to their tendency to form octahedral or tetrahedral complexes in solution. Libus and Uruska (109) thus explain the order for the stepwise formation constants of metal tetrapyridine chlorides in monochlorobenzene solution; this is the same order as that found in the present investigation for the stepwise formation constants of the metal tetrapyridine or tetrapicoline thiocyanates in either aqueous or non-aqueous solution.

It was shown in Part VI that, over the range of pyridine or picoline concentrations used in the present investigation, zinc was extracted almost exclusively as the dipyridine, di-3-picoline and di-4-picoline thiocyanate, and cobalt*, nickel and cadmium were extracted

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* Cobalt 2-picoline thiocyanate was extracted almost exclusively as the dipicolinate. The formation of the tetra-2-picoline thiocyanate of cobalt and of the other metals was shown to be hindered sterically (see Part VII-1).

almost exclusively as the tetrapyridine, tetra-3-picoline and tetra-4-picoline thiocyanates. From the above discussion of the stability orders it is reasonable to expect that the pyridine, 3-picoline and 4-picoline thiocyanates of manganese, iron and copper would be extracted mainly as the tetrapyridine and tetrapicoline complexes.

Since the estimated values of $p_4 K_{4,2}$ were available for the chloroform extraction of the pyridine, 3-picoline and 4-picoline thiocyanates of manganese, iron and copper, and for the benzene extraction of the pyridine thiocyanates of manganese, iron, cobalt, copper and zinc, it was possible to predict the position of the extraction curve for these extraction systems. The following equations were used; they were developed in Part VI:

$$\log p_4 K_{4,2} = \log D - 4 \log [P] + \log A + \log (1 + [P]K') \quad (62)$$

and

$$\log p_2 K_{2,2} = \log D - 2 \log [P] + \log A + \log (1 + [P]K') \quad (63)$$

where

$$A = \sum_{n=0} K_{o,n} [T]^{n-2} \quad (53)$$

$$K' = \frac{\sum_{n=0} K_{1,n} [T]^n}{\sum_{n=0} K_{o,n} [T]^n} \quad (36)$$

$[P]$ = concentration of free pyridine (or picoline) in the aqueous phase of the solvent-extraction system.

D = distribution ratio of the metal between the two liquid phases of the solvent-extraction system.

The thiocyanate concentration, [T], in the aqueous phase of each solvent-extraction system studied in the present investigation was 0.27 M. Values of A at this thiocyanate concentration were known for each of the metals; the values of log A are given in Appendix XVIIIC. The values of K' were known for the pyridine, 3-picoline and 4-picoline thiocyanates of cobalt, nickel, zinc and cadmium; they are in column 6 of Table LX. The values of K' were not known for the pyridine, 3-picoline and 4-picoline thiocyanates of manganese, iron and copper; with negligible error, K' was assumed to have a value of zero. From (i) the estimates of $p_4 K_{4,2}$ for the chloroform extraction of the pyridine, 3-picoline and 4-picoline thiocyanates of manganese, iron and copper; (ii) the appropriate value of log A; and (iii) two values of log D (- 1.00 and 1.00), two corresponding estimates of log [P] were obtained by using equation (62). From (i) the estimates of log $p_4 K_{4,2}$ for the benzene extraction of the pyridine thiocyanates of manganese, iron, cobalt and copper, and the estimate of log $p_2 K_{2,2}$ for the benzene extraction of zinc pyridine thiocyanate; (ii) the appropriate values of log A and K'; and (iii) two values of log D (- 1.00 and 1.00), two corresponding estimates of log [P] were obtained by using equation (62); for zinc, equation (63) was used. The data are in Table LXX. The theoretical curves for log D versus log [P] are given, in Figs. 53, 55 and 56, for the chloroform extraction of the pyridine, 3-picoline and 4-picoline thiocyanates of manganese, iron and

TABLE LXX

Predicted values of log [P] at two different values of log D

Metal (II)	Ligand	Expected number of pyridine or picoline ligands in the extracted complex	log A	K'	log $p_4 K_{4,2}$	log $p_2 K_{2,2}$	Value of log [P] at: log D = -1.0	Value of log [P] at: log D = 1.0
Manganese	Pyridine	4	2.02	0	12.59	-	-2.89	-2.39
	Pyridine*	4	"	0	10.74	-	-2.43	-1.93
	3-Picoline	4	"	0	15.05	-	-3.51	-3.01
	4-Picoline	4	"	0	15.79	-	-3.69	-3.19
Iron	Pyridine	4	1.68	0	12.28	-	-2.90	-2.40
	Pyridine*	4	"	0	10.43	-	-2.44	-1.94
	3-Picoline	4	"	0	14.74	-	-3.52	-3.02
	4-Picoline	4	"	0	15.48	-	-3.70	-3.20
Cobalt	Pyridine*	4	2.01	23.3	10.11	-	-2.28	-1.78
Copper	Pyridine	4	2.87	0	12.60	-	-2.68	-2.18
	Pyridine*	4	"	0	10.76	-	-2.22	-1.72
	3-Picoline	4	"	0	15.14	-	-3.32	-2.82
	4-Picoline	4	"	0	15.86	-	-3.50	-3.00
Zinc	Pyridine*	2	1.53	11.8	-	6.31	-2.89	-1.89

* Extraction into benzene

NOTES: (1) Values of log $p_2 K_{2,2}$ and log $p_4 K_{4,2}$ are from Table LXVIII.

(2) Values of log A are from Appendix XVIIIC.

(3) Values of K' for cobalt and zinc are from Table LX; all other values were assumed to be zero.

(4) Values of log [P] for zinc were calculated by using equation (63); all other values of log [P] were calculated by using equation (62).

FIGURES 53 TO 56

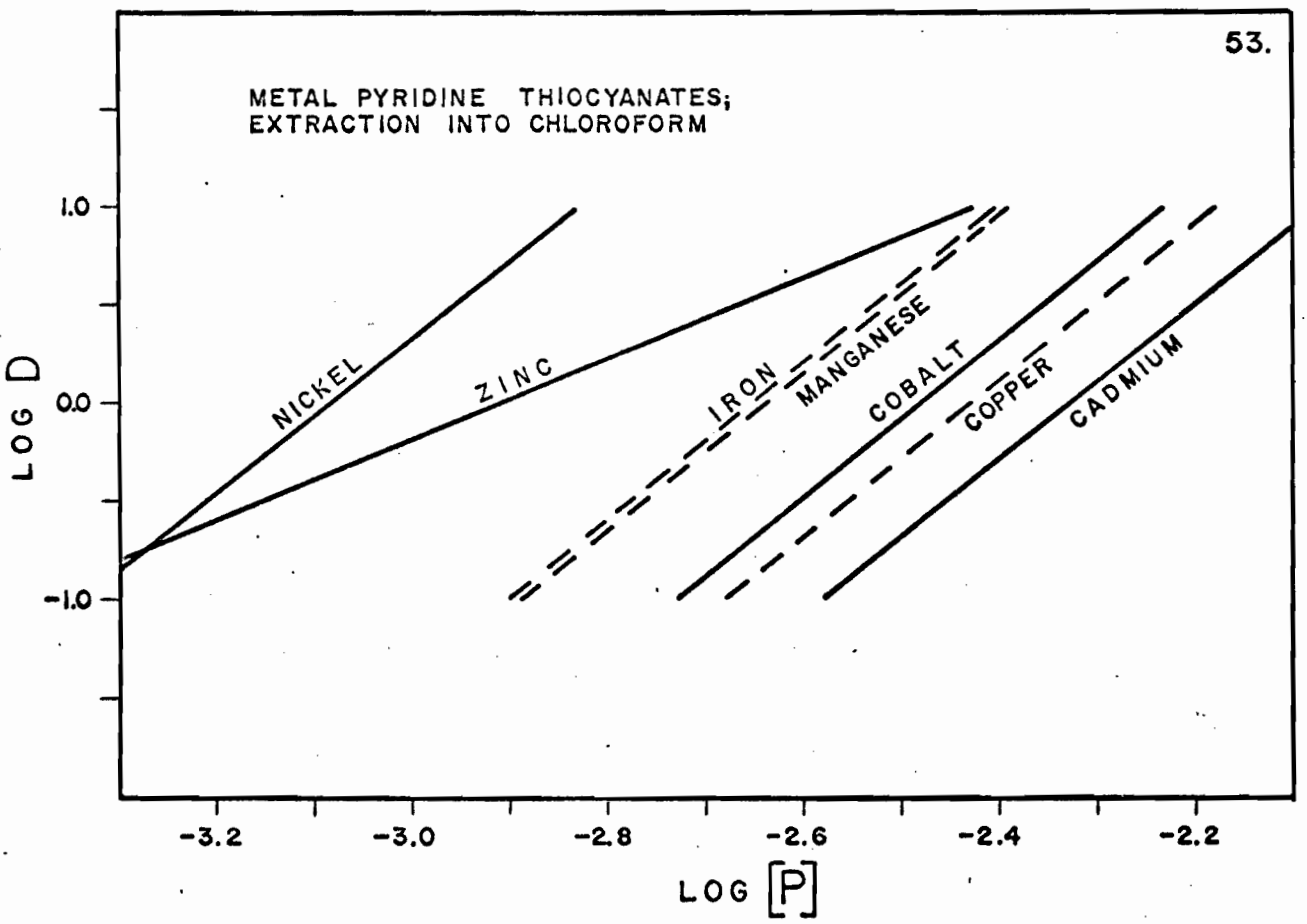
The experimental and predicted logarithmic relationships, at 25°C, between the distribution ratio of the metal, D, and the equilibrium concentration of free pyridine (or picoline) in the aqueous phase, [P].

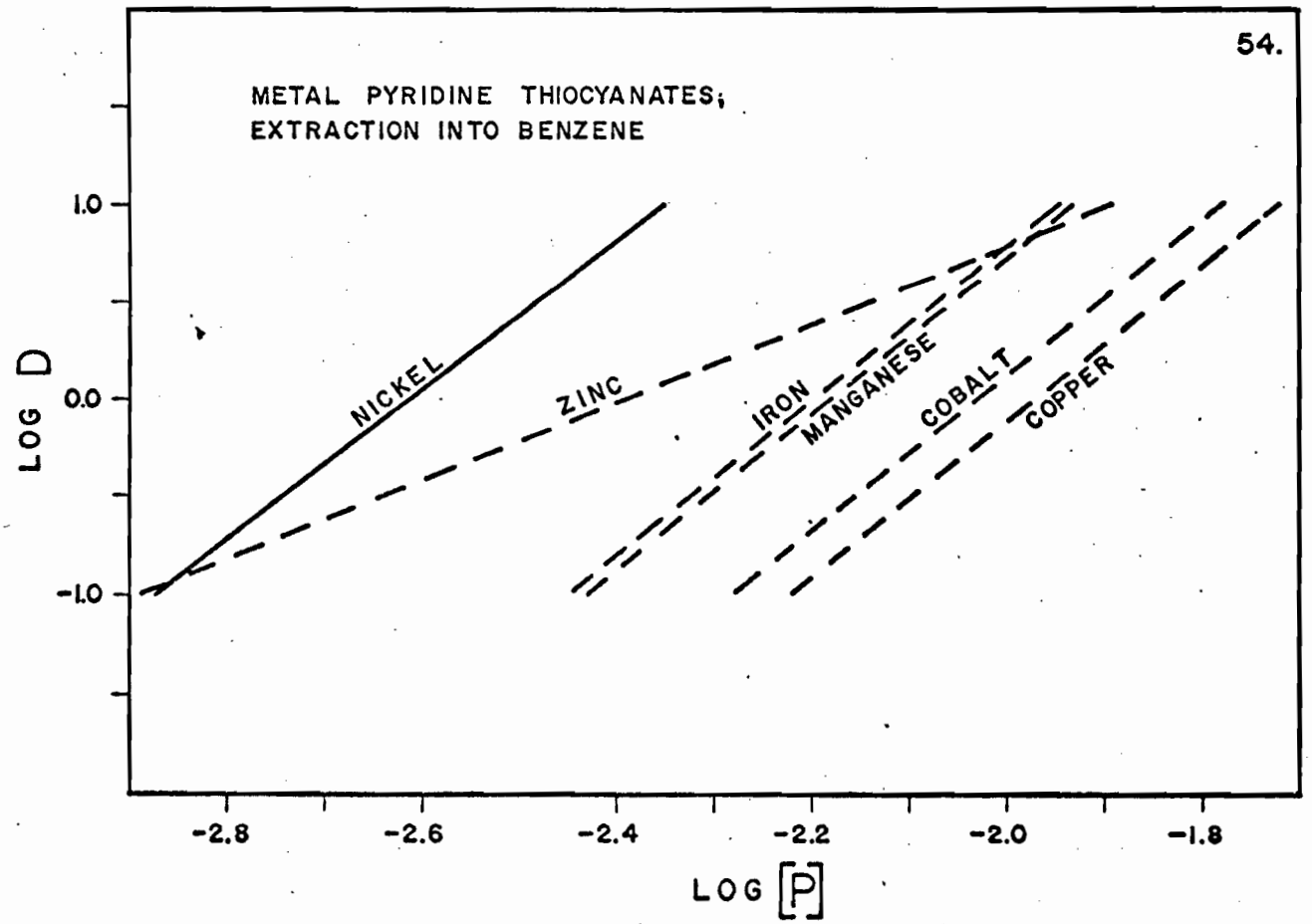
Fig. 53: Extraction of metal pyridine thiocyanates into chloroform.

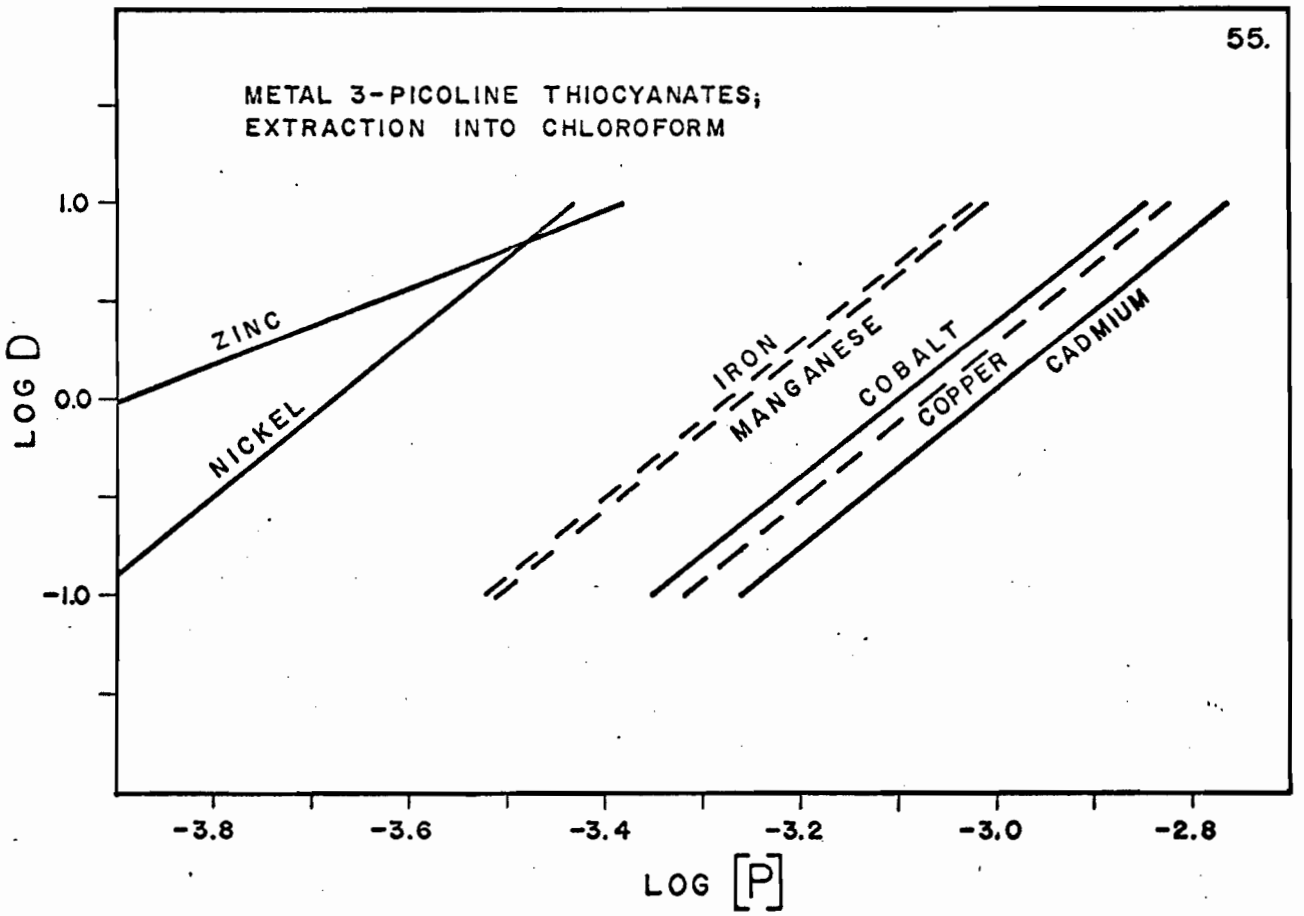
Fig. 54: Extraction of metal pyridine thiocyanates into benzene.

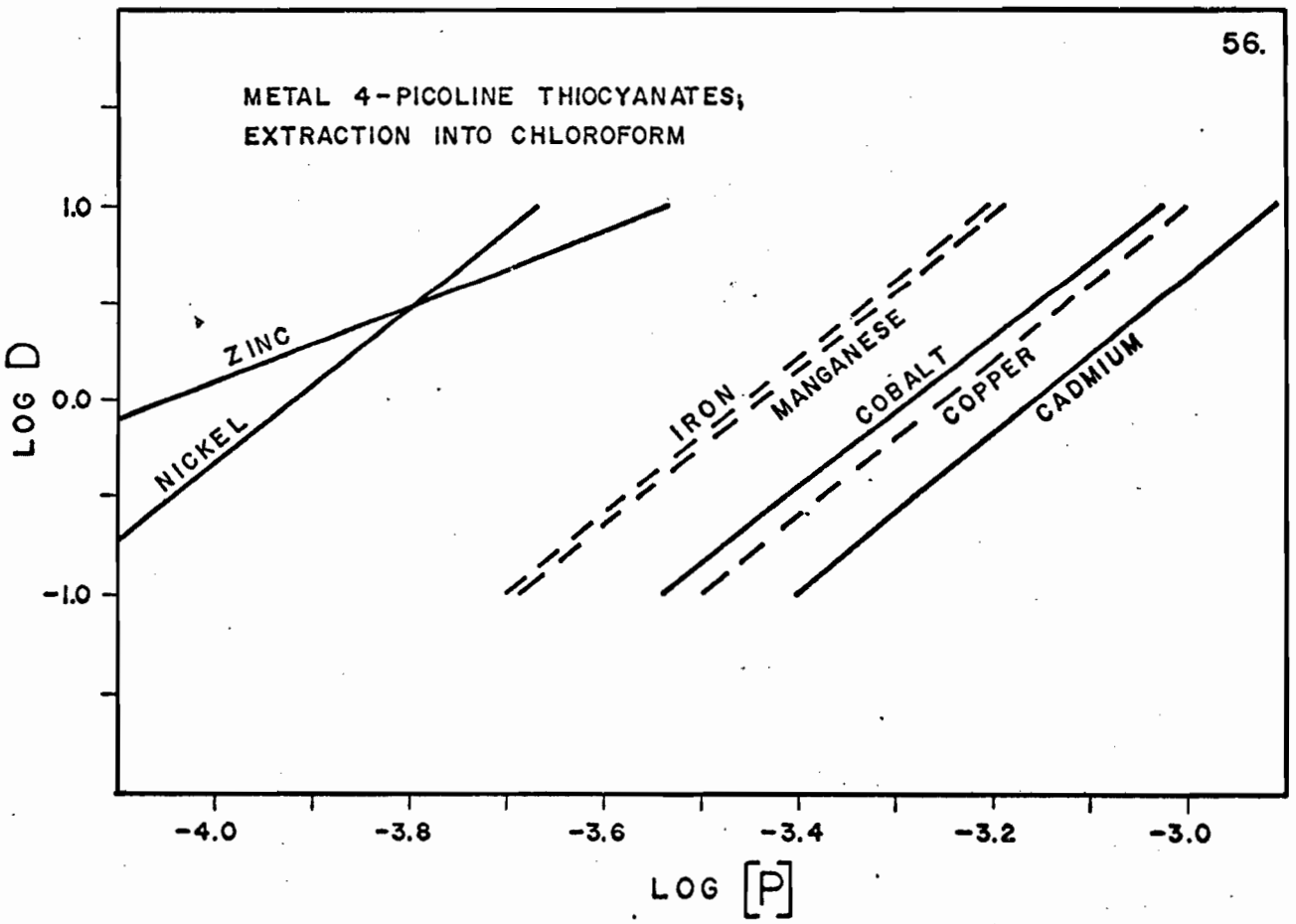
Fig. 55: Extraction of metal 3-picoline thiocyanates into chloroform.

Fig. 56: Extraction of metal 4-picoline thiocyanates into chloroform.


53.
METAL PYRIDINE THIOCYANATES;
EXTRACTION INTO CHLOROFORM
1.0
0.0
-1.0
LOG D
NICKEL
ZINC
IRON
MANGANESE
COBALT
COPPER
CADMIUM
-3.2
-3.0
-2.8
-2.6
-2.4
-2.2
LOG [P]


54.
METAL PYRIDINE THIOCYANATES;
EXTRACTION INTO BENZENE
1.0
0.0
-1.0
LOG D
NICKEL
ZINC
IRON
MANGANESE
COBALT
COPPER
-2.8
-2.6
-2.4
-2.2
-2.0
-1.8
LOG [P]


55.
METAL 3-PICOLINE THIOCYANATES;
EXTRACTION INTO CHLOROFORM
LOG D
1.0
0.0
-1.0
ZINC
NICKEL
IRON
MANGANESE
COBALT
COPPER
CADMIUM
-3.8
-3.6
-3.4
-3.2
-3.0
-2.8
LOG [P]


56.
METAL 4-PICOLINE THIOCYANATES;
EXTRACTION INTO CHLOROFORM
LOG D
1.0
0.0
-1.0
ZINC
NICKEL
IRON
MANGANESE
COBALT
COPPER
CADMIUM
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
LOG [P]

copper, and in Fig. 54 for the benzene extraction of the pyridine thiocyanates of manganese, iron, cobalt, copper and zinc. The plots of log D versus log [P] found experimentally are also included for comparison.

These curves shown in Figs. 53 to 56 indicate immediately the feasibility of analytical separations of these metals by means of the pyridine (or picoline) thiocyanate solvent-extraction system. The solvent-extraction separation of some of the metals studied experimentally in the present investigation is considered below in Part VII-3.

2-3. Effect of the Solvent

Both chloroform and benzene were used to extract nickel pyridine thiocyanate from aqueous 0.3-M potassium thiocyanate solutions containing excess pyridine. The values of k_4, p, $p_2 K_{2,2}$ and $p_4 K_{4,2}$ for these extraction systems* are in Table LXXI. It is the purpose of the present sub-Section to examine the effect of a change of solvent on these values.

If it is assumed that the formation constants in the aqueous phase are not influenced by a change in the solvent comprising the organic phase, then

$$\frac{p_4 K_{4,2}}{{}^*p_4 {}^*K_{4,2}} = \frac{p_4}{{}^*p_4} = 72$$

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* Throughout the present sub-Section, an asterisk superscript will denote values for the case where benzene is the solvent; values without the asterisk superscript will denote values for the case where chloroform is the solvent.

TABLE LXXI

Values of $p_4 K_{4,2}$, $p_2 K_{2,2}$, k_4 and p for the extraction of nickel pyridine thiocyanate into chloroform and into benzene at 25°C

Chloroform		Benzene	
$p_4 K_{4,2}$	$= 3.42 \times 10^{14}$	$*p_4 *K_{4,2}$	$= 4.77 \times 10^{12}$
$p_2 K_{2,2}$	$= 4.3 \times 10^{3}$	$*p_2 *K_{2,2}$	$= 3.5 \times 10^{2}$
k_4	$= 4.0 \times 10^{8}$	$*k_4$	$= 1.6 \times 10^{9}$
p	= 14.1	*p	= 2.93

NOTES: (1) The data are from Table LXVIII.

(2) An asterisk superscript denotes values for the case where benzene is the solvent; values without a superscript are for the case where chloroform is the solvent.

(3) $$p_m = \frac{[MP_m T_2]_o}{[MP_m T_2]} \quad ; \quad m = 2, 4 \qquad (65)$$

$$K_{m,2} = \frac{[MP_m T_2]}{[M][P]^m [T]^2} \quad ; \quad m = 2, 4 \qquad (66)$$

$$k_4 = \frac{[MP_4 T_2]_o}{[MP_2 T_2]_o [P]_o^2} = \frac{p_4 K_{4,2}}{p_2 K_{2,2}} \cdot \frac{1}{p^2} \qquad (64)$$

(4) p is the partition coefficient of pyridine (or picoline) between the two phases of the solvent-extraction system.

and

$$\frac{p_2 K_{2,2}}{{}^*p_2 {}^*K_{2,2}} = \frac{p_2}{{}^*p_2} \doteq 12$$

It is seen that the partition coefficients of nickel dipyridine thiocyanate and nickel tetrapyridine thiocyanate are larger when chloroform, rather than benzene, is the solvent. In addition, from the ratio of partition coefficients of free pyridine

$$\frac{p}{p^*} = 4.8$$

it is seen that pyridine is more readily extracted into chloroform than into benzene.

The ratio of the stepwise formation constant of nickel tetrapyridine thiocyanate in chloroform to that in benzene is

$$\frac{k_4}{{}^*k_4} = 0.25$$

from which it is evident that nickel tetrapyridine thiocyanate is more stable in benzene than in chloroform, at any given concentration of free pyridine in the organic phase. It has been shown (68) that the degree of solvation of a polar solute decreases with the dielectric constant. Chloroform and benzene have dielectric constants of 4.81 and 2.27, respectively (70). It is therefore expected that solvation of pyridine and of nickel dipyridine thiocyanate will be more extensive in chloroform than in benzene. Nickel tetrapyridine thiocyanate may be expected to be nearly non-polar, since it is a symmetrical molecule.

Therefore, solvation of this complex in non-aqueous solution would be expected to occur to a lesser degree than for the nickel dipyridine thiocyanate complex. However, the energy of interaction of pyridine with nickel dipyridine thiocyanate will be greater in benzene than in chloroform because the dielectric constant of benzene is lower than that of chloroform.

It has been shown (68) that the energy required to extract a polar molecule from water into an immiscible organic solvent decreases with increasing dielectric constant. Thus, the partition coefficients of pyridine (p) and nickel dipyridine thiocyanate (p_2) are greater when chloroform, rather than benzene is the solvent. That the partition coefficient of nickel tetrapyridine thiocyanate is greater when chloroform rather than benzene is the solvent may be due to the existence of a dipole induced by the chloroform; such a dipole would not be induced by benzene.

2-4. Effect of pH

The addition of pyridinium (or picolinium) chloride to the aqueous phase of a metal pyridine (or picoline) thiocyanate extraction system was shown in Part VI-4 to have no measurable effect upon either the nature of the extracted species or the distribution ratio of the metal. However, the presence of pyridinium (or picolinium) chloride in the aqueous phase resulted in a small decrease* in the concentration of complexed pyridine (or picoline) in the aqueous phase. It is not clear why this effect should have occurred.

2-5. Effect of the Metal Concentration

An increase in the total metal concentration of the nickel and cobalt pyridine thiocyanate extraction systems was shown in Part VI-1 to result in an approximately proportional increase in the concentration of complexed pyridine in the aqueous phase. Moreover, the

* The effect of pyridinium (or picolinium) chloride was found to be small in comparison to the effect either of changing the metal in a given extraction system or of the substitution of a picoline for pyridine.

complexed pyridine in the aqueous phase was shown to be present mainly as a mixed metal pyridine thiocyanate complex. Thus, the shift of an extraction curve to a lower concentration of total pyridine in the aqueous phase on decreasing the metal content can be accounted for by postulating the existence of mixed metal pyridine thiocyanate complexes in the aqueous phase.

It was shown in Part VI-4 that, at a given concentration of free pyridine in the aqueous phase, the distribution ratio of the metal was independent of the total metal concentration of the extraction system. From this fact the following conclusions are drawn: (1) the existence of polynuclear species of the metal complex in the organic phase was unlikely, since the distribution ratio was shown (see equation (15)) to be independent of the metal concentration only in the absence of such species; (2) no appreciable hydrolysis of the metal ion occurred in the aqueous phase; and (3) the activity coefficients of the various components of each phase remained essentially constant throughout the range of concentrations used.

2-6. Effect of the Extraction Temperature

An increase in the temperature of the cobalt and nickel pyridine thiocyanate extraction systems was shown to result in a decrease in the distribution ratio of the metal (see Figs. 10 and 9, respectively). In addition, it was shown in Part VI that the cobalt and nickel pyridine thiocyanates were extracted almost exclusively as the tetrapyridinates. For such cases, the distribution ratio of the metal, D, may be written as follows:

$$\log D = \log p_4 K_{4,2} + 4 \log [P] - \log (A + f [P]) \qquad (59)$$

where p_4 is the partition coefficient of the metal tetrapyridine thiocyanate, $K_{4,2}$ is the overall formation constant of the metal tetrapyridine thiocyanate in aqueous solution, and $[P]$ is the concentration of free pyridine in the aqueous phase. The parameters A and $f[P]$ are defined by equations (53) and (54), respectively; they will not be considered here for the following reasons: (1) both A and $f[P]$ are expected to have only very slightly smaller values as the temperature of the extraction system is raised; and (2) any decrease in the values of A and $f[P]$ would not explain the observed decrease in the distribution ratio with increasing temperature.

Thus, a decrease in the distribution ratio, D, with increasing temperature will be due mainly to a decrease in the product $p_4 K_{4,2}$ and/or a decrease in the free pyridine concentration of the aqueous phase, $[P]$. It is expected that p_4 will increase and that $K_{4,2}$ will decrease, with increasing temperature. In addition, the partition coefficient of pyridine, p, is also expected to increase with temperature. An increase in p would lead to a lower concentration of free pyridine in the aqueous phase. Since the exact effect of temperature on these opposing factors is unknown, so is the exact reason for the observed decrease in the distribution ratio with increasing temperature*.

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* It is worth noting that, if $p_4 K_{4,2}$ and $\log (A + f[P])$ are assumed to be independent of temperature, then by using equation (59) it may be shown that a one percent per $^{\circ}C$ increase in the partition coefficient of pyridine (a one percent per $^{\circ}C$ decrease in the free pyridine concentration of the aqueous phase) will provide nearly the same decrease in the distribution ratio of cobalt with increasing temperature as shown in Fig. 10.

3. Analytical Applications of the Extraction Data

The percent extraction of a given metal into chloroform is a unique function of the equilibrium concentration of pyridine (or picoline) in the aqueous phase, for a metal pyridine (or picoline) thiocyanate extraction system. The curves for the percent extraction of the cobalt, nickel, zinc and cadmium pyridine thiocyanates into chloroform as a function of the total equilibrium concentration of pyridine in the aqueous phase are in Fig. 57. Similar curves, where 4-picoline rather than pyridine was used as the complexing agent, are in Fig. 58.

It was shown in Part V-4 that a reduction in the total concentration of the metal* in the pyridine thiocyanate system resulted in a small displacement of the extraction curve to the left, and that this displacement was small relative to the effect of changing the metal. It was also shown in Part V-4 that the addition of pyridinium (or picolinium) chloride to the extraction system resulted in a small displacement of the extraction curve to the left, and this displacement was small relative to the effect of changing the metal. The presence of pyridinium (or picolinium) chloride was an important variable for study because it allowed a reduction in the pH of the aqueous phase to a level where hydrolysis would be unlikely. It is also a potentially-useful buffer system, namely pyridine-pyridinium (or picoline-picolinium), in practical analyses involving the present solvent-extraction systems.

From Fig. 57 it is evident that for values of the total

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* In Part V-2 it was reported that above the following metal concentrations, precipitation of the metal pyridine (or picoline) thiocyanate may occur in the extraction systems: nickel, 5×10^{-3}M; cobalt, 1.3×10^{-3}M; zinc, 5×10^{-3}M; cadmium, 1×10^{-3}M.

FIGURE 57

Percent extraction of metals into chloroform at 25°C, versus the total equilibrium concentration of pyridine in the aqueous phase.

Equilibrium concentration of potassium thiocyanate in the aqueous phase: 0.3 M.

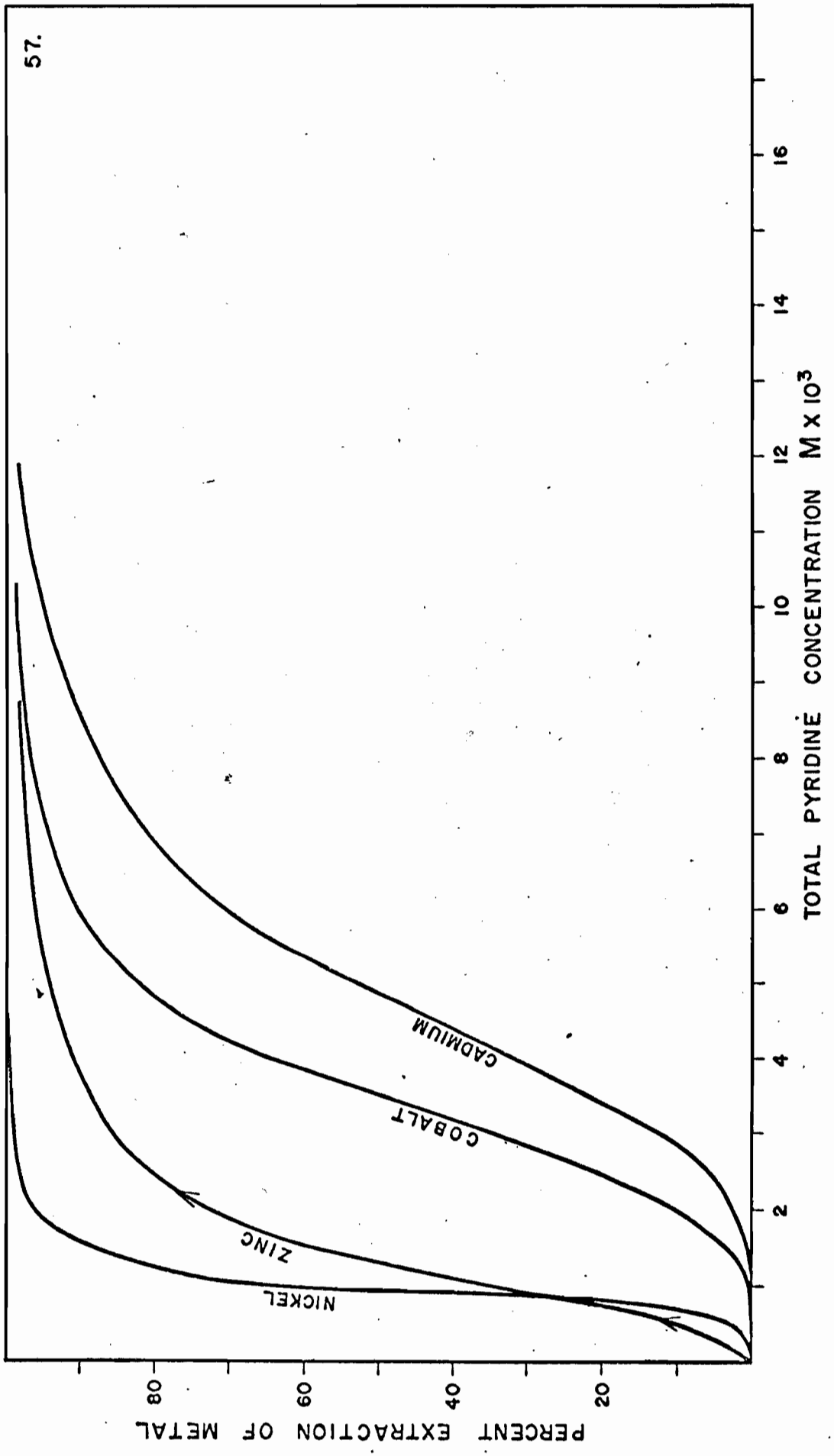
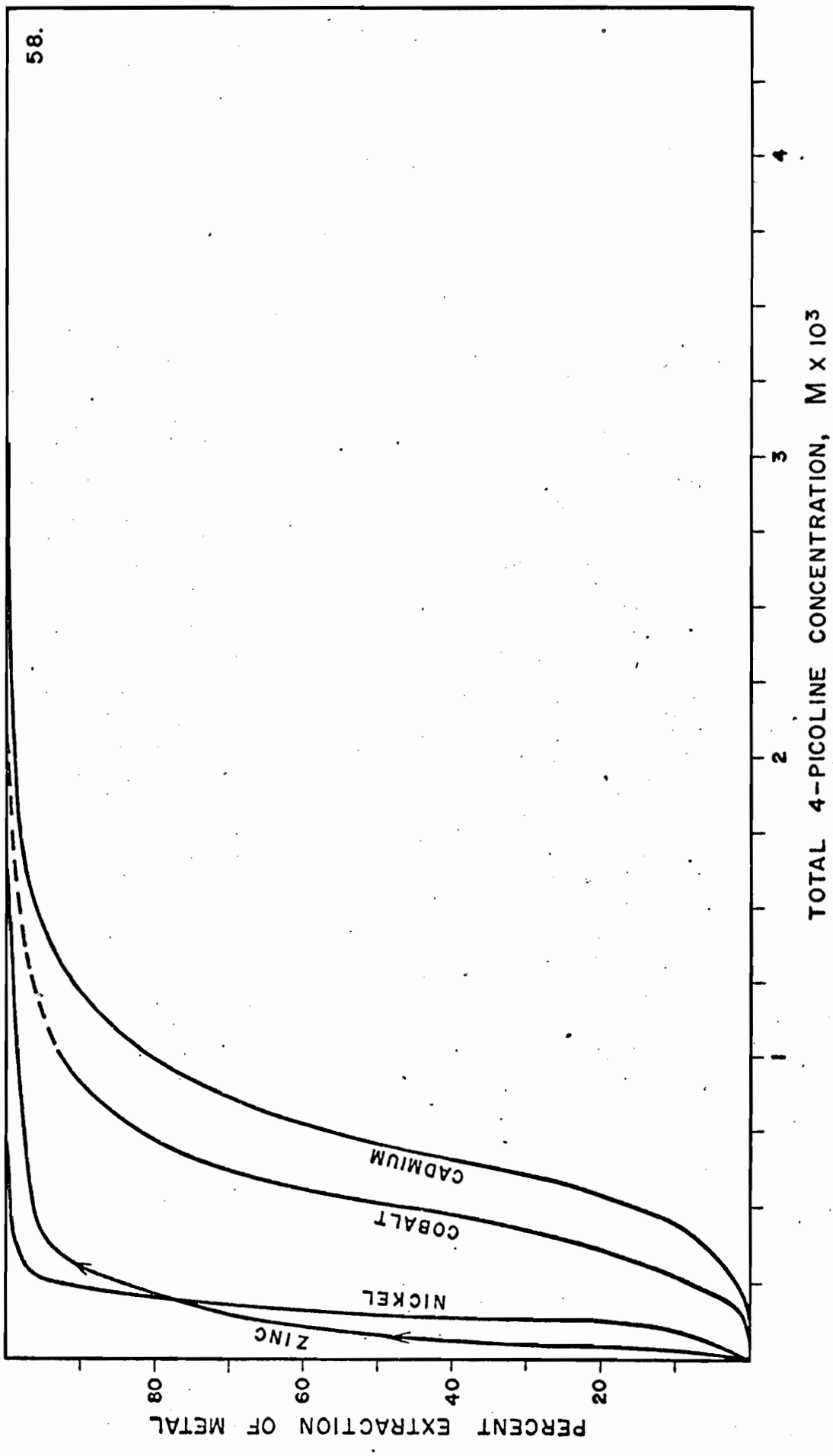

57.
PERCENT EXTRACTION OF METAL
20
40
60
80
TOTAL PYRIDINE CONCENTRATION M x 10³
2
4
6
8
10
12
14
16
NICKEL
ZINC
COBALT
CADMIUM

FIGURE 58

Percent extraction of metals into chloroform at 25°C, versus the total equilibrium concentration of 4-picoline in the aqueous phase (0.001-M picolinium chloride added).

Equilibrium concentration of potassium thiocyanate in the aqueous phase: 0.3 M.

NOTE: The dotted line indicates data for extractions where picolinium chloride was not added.


58.
PERCENT EXTRACTION OF METAL
20
40
60
80
ZINC
NICKEL
COBALT
CADMIUM
1
2
3
4
TOTAL 4-PICOLINE CONCENTRATION, M X 10³

pyridine concentration in the aqueous phase between 1.75×10^{-3}M and 2.25×10^{-3}M, a separation of either cobalt or cadmium from zinc or nickel may be made. At these two pyridine concentrations, respectively, the following percentages of the metal would be extracted: nickel, 93 and 97; zinc, 67 and 77; cobalt, 7 and 15; cadmium, 1.5 and 4. Even by using batchwise extractions, the minor components (cobalt and/or cadmium) of the chloroform extract could be largely removed by back extraction with a 0.3-M aqueous thiocyanate solution*.

The feasibility of the separation of nickel from cobalt and of zinc from cadmium are of particular interest in view of the very common natural occurrence of these pairs of metals together.

An example of how the pyridine thiocyanate extraction system may be utilized to separate two metals is given in the following procedure:

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* The equilibrium concentration of pyridine in both the organic and aqueous phases will be about 7 percent less than after the first extraction due to the separation of that aqueous phase and subsequent re-equilibration with an equal volume of the pyridine-free thiocyanate solution. Therefore, if the concentration of pyridine in the aqueous phase was 2.25×10^{-3}M after the first extraction, its concentration after the back extraction would be about 2.1×10^{-3}M. At this latter concentration the following percentages of the metals are extracted: nickel, 97; zinc, 74; cobalt, 12; cadmium, 3.0. If 1 mg each of the metals were initially taken, it may be readily calculated that, after the back extraction with 0.3-M thiocyanate, the metal content (in mg) of the chloroform phase would be as follows: nickel, 0.94; zinc, 0.57; cobalt, 0.02; cadmium, 0.001.

Procedure: To separate nickel from cadmium present in a dilute (0.01 M) hydrochloric acid solution, dilute the solution with water until the concentrations of nickel and cadmium do not exceed 0.005 M and 0.001 M, respectively, in order to prevent the formation of solid phases. Neutralize this solution with pyridine to pH 4 ± 0.2. Make the solution 0.3 M* in potassium thiocyanate. Then add an amount of pyridine** such that after equilibration at 25.0°C*** with an equal volume of chloroform, the aqueous phase will be between 1.75×10^{-3}M and 2.25×10^{-3}M in pyridine. Add a volume of chloroform equal to that of the aqueous phase. Extract at 25°C for 2 minutes. Under these conditions, between 93 and 97 percent of the nickel will be extracted, together with between 1.5 and 4 percent of the cadmium. Separate the chloroform phase and shake it for 2 minutes at 25.0°C with an equal volume of 0.3-M potassium thiocyanate. The chloroform phase will now contain between 85 and 94 percent of the total nickel and between 0.01 and 0.12 percent of the total cadmium.

The effect of repeated back extractions together with the

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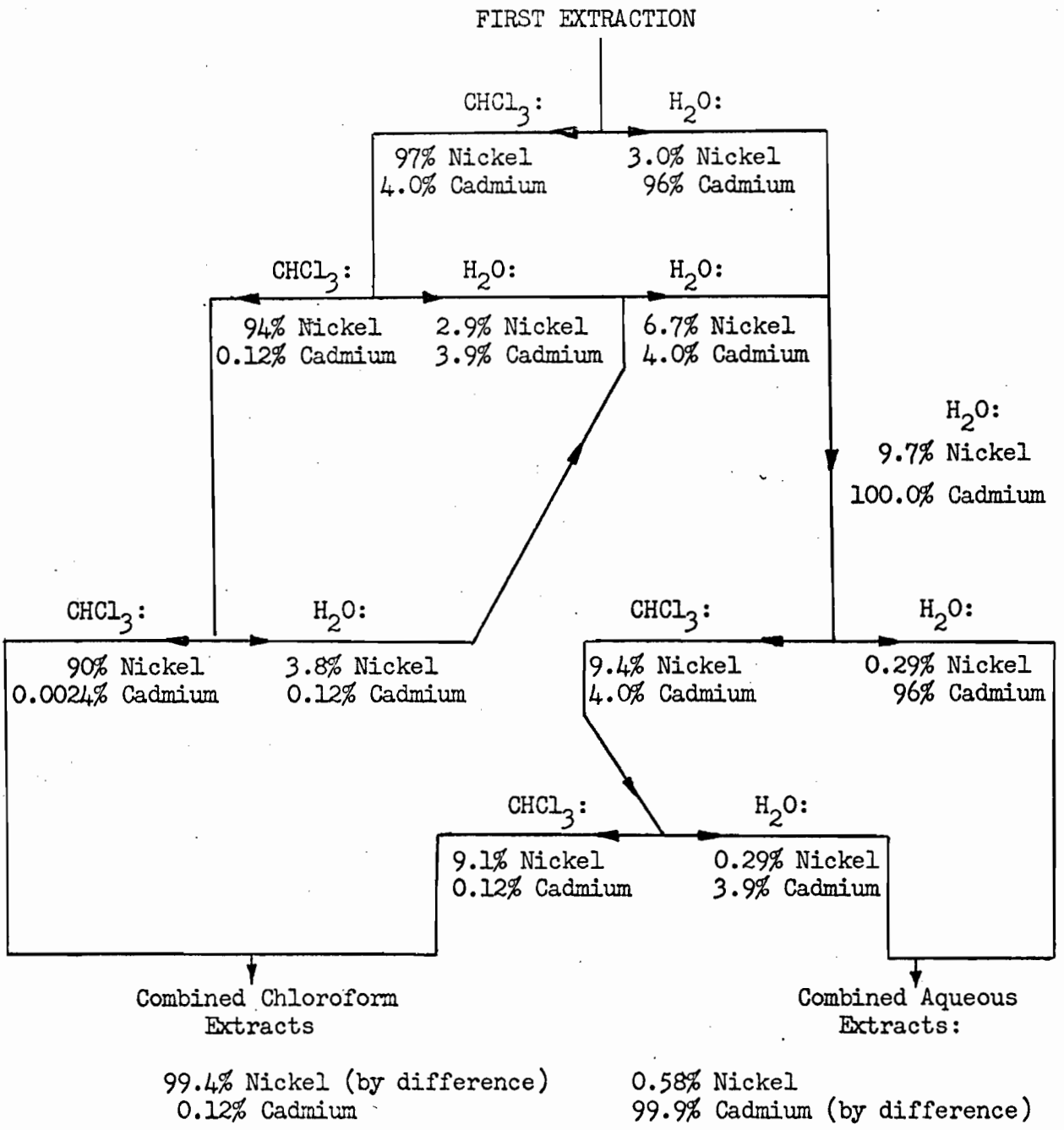
* It was shown in Appendix XVIIIC that a 2 percent change in the thiocyanate concentration of the aqueous phase changed the distribution ratio of the metal by about one percent. Therefore a 10 percent change in that thiocyanate concentration will affect the distribution ratio by about 5 percent. A 5 percent change in the distribution ratio will only change the percent extraction by 1.3 percent or less.

** This quantity is readily calculated by using the known partition coefficient of pyridine (14.1) and the approximate concentrations of the metals present.

*** It is seen from Figs. 9 and 10, respectively, that the distribution ratios of nickel and cobalt pyridine thiocyanates decrease by about 10 percent per degree increase in temperature. The percent extraction varies by less than 2.4 percent for a 10 percent increase (or decrease) in the distribution ratio of the metal. Therefore, for any temperature between 24°C and 26°C, the percent extraction of the metal will have the same value as that at 25.0°C to within ± 2.4 percent.

effect of combining the aqueous extracts and re-extracting are indicated in the flow diagram below.



NOTES: (1) The following conditions apply to the flow diagram: (i) all extractions involve equal phase volumes; (ii) all back extractions are carried out with 0.3-M potassium thiocyanate; (iii) for all extractions with fresh chloroform, the pyridine

concentration of the aqueous phase is adjusted such that, after equilibration with that chloroform, the concentration of pyridine in the aqueous phase is 2.25×10^{-3}M.

(2) Each percentage given is that of the total metal in the original sample.

It is seen from the flow diagram that about 5 extractions are required to obtain a nearly-quantitative separation of the two metals. The degree of separation at any weight ratio of nickel to cadmium is obtained from the percentages given for the combined extracts; when this ratio is greater than unity, the combined chloroform extracts and the combined aqueous extracts both contain a higher proportion of nickel; when this ratio is less than unity, the reverse is true.

It is evident from Fig. 58, where 4-picoline is substituted for pyridine, that a similar procedure could be devised for the separation of these and other metals by using the 4-picoline thiocyanate system. The selectivity of the extraction is approximately the same with either reagent.

Less 4-picoline than pyridine is required to extract a given amount of a given metal. However, pyridine may be preferred for the following reasons: (1) it is more readily available from chemical supply houses; (2) it is more easily purified, and the proof of its purity involves a simpler procedure (see Part II-2-3); and (3) it is much cheaper*.

The separation of these metals is also feasible by means of continuous extraction using a column. The equations given by Weissburger

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* The 1966 J.T. Baker chemical catalogue quotes the following per pound prices for their best grade: pyridine, $2.30; 2-picoline, $3.00; 3-picoline, $7.08; 4-picoline, $7.26.

(125) were used to calculate the number of theoretical stages required for the column separation of mixtures of zinc and nickel by means of their selective extraction into chloroform as pyridine thiocyanate complexes. These two metals were selected because they are the most difficult pair to separate, by solvent extraction, within the group of four metals studied (see Figs. 57 and 58). Therefore other pairs of metals could be separated with the same degree of completeness by using a smaller number of theoretical stages.

The descriptions of the two mixtures considered, together with the calculated* numbers of theoretical stages are given in Table LXXII.

The data illustrated by Figs. 57 and 58 are equilibrium data. Presentation of equilibrium data avoids the shortcoming inherent in previously published procedures, namely that they give only initial concentration values. The data in Figs. 57 and 58 thus provide the basis for general procedures. That is, the feasibility of separating any pair of metals is readily evaluated by referring to a single figure, such as Fig. 57. It inherently contains the conditions for the separation of metals in any system that might be encountered. Therefore, they constitute a significant advance over all previously published data, such as those contained in the procedures of Forsythe, Magee and Wilson (14,15,102) or Welcher (104) which give instructions arrived at empirically.

The pyridine thiocyanates of divalent manganese, iron, cobalt, nickel, copper, zinc, palladium and cadmium are known to extract (see Part I-1). In the present investigation, the extraction curves for the

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* Instantaneous, 100 percent stage efficiency was assumed.

TABLE LXXII

The calculated number of theoretical stages for the continuous column extraction of mixtures of nickel and zinc by means of their selective extraction into chloroform as pyridine thiocyanate complexes

EXAMPLE 1					
Metal	Metal in sample solution, mg	Distribution ratio of metal*	Desired weight of metal in phase, mg		Number of theoretical stages
			H_2O	$CHCl_3$	
Nickel	0.0100	300.	0.00001	0.00999	10
Zinc	10.0000	11.	9.99999	0.00001	
EXAMPLE 2					
Metal	Metal in sample solution, mg	Distribution ratio of metal*	Desired weight of metal in phase, mg		Number of theoretical stages
			H_2O	$CHCl_3$	
Nickel	10.0000	0.06	9.99999	0.00001	32
Zinc	0.0100	0.18	0.00001	0.00999	

* Values for the distribution ratios of the metals (as pyridine thiocyanates) between chloroform and aqueous 0.3-M potassium thiocyanate solutions at 25°C were read, for nickel and zinc, respectively, from Figs. 11B and 18B. For examples 1 and 2 the total pyridine concentration in the aqueous phase required to give those distribution ratios was 4.0×10^{-3}M and 0.5×10^{-3}M, respectively.

NOTE: The number of theoretical stages was calculated from the equations of Weissburger (125). The calculations assumed instantaneous, 100 percent stage efficiency.

cobalt, nickel, copper*, zinc and cadmium pyridine thiocyanates were determined. The experimental determination of the extraction of manganese, iron and palladium pyridine thiocyanates as a function of the equilibrium concentration of pyridine might permit useful procedures to be devised for their separation from one another and from other metals.

Many metals are precipitated as hydrated oxides from aqueous solution by the addition of excess pyridine; these precipitates apparently are insoluble in chloroform. Iron (III), aluminum (III), uranium, zirconium, tin, tellurium and bismuth form (105) such precipitates, as do (104) chromium (III), titanium, antimony, thorium, cesium, lanthanum, neodymium, praseodymium and lead. Mercury (106) forms a water-soluble complex ion $HgCl_2(CNS)_2$ in the presence of thiocyanate; it is not affected by excess pyridine. Ruthenium (15), and rhodium and platinum (102) also form soluble complexes in aqueous solutions containing pyridine and thiocyanate; these complexes do not extract into non-aqueous solvents. Therefore, provided that co-precipitation is negligible, each of the above-named metals may be quantitatively separated from divalent manganese, iron, cobalt, nickel, copper, zinc, palladium and cadmium by extracting the latter metals into chloroform as their pyridine thiocyanates. The usefulness of such separations appears not to have been evaluated.

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* Due to precipitation of copper under conditions of incomplete extraction it was not possible to study in detail the extraction of copper pyridine thiocyanate as a function of the pyridine concentration (see Part V-2).

4. Suggestions for Further Work

I. The practical aspect of the present investigation was to illustrate that various metals could be separated from one another by means of the pyridine (or picoline) thiocyanate extraction system. Obviously, the selective extraction and complete separation of one metal from an aqueous solution containing several metals can be made in one solvent-extraction operation, provided that extraction curves are sufficiently far apart. If the extraction curves are not widely separated then, as for the pyridine or picoline thiocyanate extraction system, replicate extractions are necessary, together with a suitable adjustment of the pyridine (or picoline) concentration between extractions.

In order to increase the separation of the extraction curves for the different metals, only a few variables are available. It is suggested that the effect of each of the following variables on the separation of the extraction curves be evaluated:

(1) The effect of alkyl or aryl-substituted pyridine ligands causing a partial steric hindrance in the formation of a metal complex may be to increase the selectivity with which different metals are extracted. Such ligands would be expected to accent the difference between the formation constants of the extractable complexes for each metal.

(2) The substitution of a ligand such as selenocyanate for thiocyanate may also result in a steric effect similar to that described above.

(3) The use of a smaller or larger initial concentration of thiocyanate in the aqueous phase may lead to increased selectivity through changes in the equilibrium composition of the aqueous phase. It

should be noted, however, that a complication would arise if a thiocyanate concentration much smaller than that used in the present investigation (0.3 M) were used; the depletion of the thiocyanate concentration both by extraction of the metal complex and by the formation of thiocyanate complexes of the metal (mixed or otherwise) in the aqueous phase would have to be corrected for if valid comparisons of different systems were to be made. Such a complication could be avoided by the use of a correspondingly smaller total concentration of the metal in the extraction system.

(4) Although the metal pyridine and picoline thiocyanate extraction systems have been shown to reach equilibrium quite rapidly, a study of the rate of equilibration may lead to extraction procedures which exploit the differences in such rates to obtain better selectivity.

(5) The distribution ratios of the cobalt and nickel pyridine thiocyanates have been shown to have a different dependence upon the extraction temperature. A more extensive study of the dependence of the distribution ratio upon temperature may also lead to greater selectivity.

II. It has been shown that the pyridine, 3-picoline and 4-picoline thiocyanates of cobalt, nickel and cadmium are extracted almost exclusively as the tetrapyridinates or tetrapicolinates over the range of pyridine or picoline concentrations used in the present investigation. In addition, the 2-picoline thiocyanate of cobalt, and the pyridine, 3-picoline and 4-picoline thiocyanates of zinc have been shown to be

extracted almost exclusively as the dipyridinate or dipicolinate. The product of the partition coefficient of the extracted complex (p_2 or p_4) and the overall formation constant of that complex in the aqueous phase ($K_{2,2}$ or $K_{4,2}$) has been found. From experimental data, either $p_2 K_{2,2}$ or $p_4 K_{4,2}$ had been found for each of the metal pyridine or picoline thiocyanates. The experimental evaluation of the unknown products (either $p_2 K_{2,2}$ or $p_4 K_{4,2}$) then would lead directly to the stepwise formation constants, k_4, of the metal tetrapyridine or tetrapicoline thiocyanates in the organic phase:

$$k_4 = \frac{p_4 K_{4,2}}{p_2 K_{2,2}} \frac{1}{p^2} \qquad (64)$$

where p is the partition coefficient of the pyridine or picoline ligand. Finally, the experimental evaluation of the partition coefficients p_2 and p_4 then would allow the formation constants $K_{2,2}$ and $K_{4,2}$ to be calculated.

It is suggested that experiments be devised to evaluate the unknown products (either $p_2 K_{2,2}$ or $p_4 K_{4,2}$) and the partition coefficients p_2 and p_4. For this purpose, both much higher and much lower concentrations of pyridine or picoline than those in the present investigation must be used. As indicated in Part VI (see equations (50) to (58)), a study of the distribution ratio of the metal both at these higher and lower concentrations of pyridine or picoline should lead to values of p_2 and p_4 and for the unknown values of either $p_2 K_{2,2}$ or $p_4 K_{4,2}$.

The experimental work of the present investigation was not initially directed at the determination of these values for the reason that analytical separations of the metals could be made without resort to these

higher or lower concentrations of pyridine or picoline.

However, to carry out the experiments suggested above it will be necessary to develop sensitive analytical methods to determine both very large and very small distribution ratios of the metals; for this purpose, the development of radiochemical methods of analysis is suggested. To determine pyridine or picoline concentrations much smaller than those used in the present investigation, new analytical methods will be required; such methods are unknown at the present time.

III. In Part VI the predicted positions of the extraction curves were given for the pyridine, 3-picoline and 4-picoline thiocyanates of manganese, iron and copper. It is suggested that these positions be determined experimentally. Their determination then would lead to analytical procedures for the separation of a much larger group of metals.

IV. A study of the effect of the organic solvent on the partition coefficients of the extracted metal pyridine or picoline thiocyanate complexes would be an area for profitable research, since solvation effects could be studied directly.

V. It is seen from the data in Table LXV that the pK_a value of a pyridine base having an alkyl group in a given position on the ring is nearly independent of the magnitude of the alkyl group. Such bases then might be expected to form, with a metal thiocyanate, complexes having the same formation constants but different partition coefficients. Such a study then could lead to an understanding of the factors which deter-

mine the magnitude of a partition coefficient.

5. Summary, and Claim to Original Research

The pyridine, 3-picoline and 4-picoline thiocyanates of cobalt, nickel, zinc and cadmium, and the 2-picoline thiocyanate of cobalt were studied, at 25°C, in equilibrated solvent-extraction systems.

The distribution ratio of the metal was measured as a function of the total equilibrium concentration of pyridine or picoline in the aqueous phase. The ionic strength of the aqueous phase was maintained essentially constant by the use of 0.3-M potassium thiocyanate. Chloroform was used to extract each of the metal pyridine and picoline thiocyanate complexes. Benzene was also used to extract nickel pyridine thiocyanate.

A mathematical treatment of the extraction data showed that the pyridine, 3-picoline and 4-picoline thiocyanates of cobalt, nickel and cadmium were extracted almost exclusively as the tetrapyridinates and tetrapicolinates; the pyridine, 3-picoline and 4-picoline thiocyanates of zinc and the 2-picoline thiocyanate of cobalt were extracted almost exclusively as the dipyridinates and dipicolinates. This mathematical treatment gave, for those complexes extracted primarily as the tetrapyridinate or tetrapicolinate, the product $p_4 K_{4,2}$ of the partition coefficient, p_4, and the overall formation constant in the aqueous phase, $K_{4,2}$; for those complexes extracted primarily as the dipyridinate or dipicolinate, the product $p_2 K_{2,2}$ of the partition coefficient, p_2, and the overall formation constant in the aqueous phase, $K_{2,2}$, was found.

A thermodynamic treatment of literature data gave estimates for the stepwise formation constants of the metal tetrapyridine and tetrapicoline thiocyanates in the organic phase. This treatment also provided estimates of the unknown products (either $p_2 K_{2,2}$ or $p_4 K_{4,2}$) for those metal pyridine and picoline thiocyanate extraction systems studied experimentally. In addition estimates were obtained of both $p_2 K_{2,2}$ and $p_4 K_{4,2}$ for the pyridine and picoline thiocyanates of manganese, iron and copper.

Both the partition coefficients (p_2 or p_4) and the overall formation constants in the aqueous phase ($K_{2,2}$ or $K_{4,2}$) were found, for a given metal, to increase in the order pyridine < 3-picoline < 4-picoline.

The order of the overall formation constants in the aqueous phase and of the stepwise formation constants in the organic phase was found, for the various metals, to be the same for any one of the pyridine or picoline ligands.

The substitution of benzene for chloroform as solvent was found to result in smaller values of p_2 and p_4.

In experiments where different total concentrations of the metal were used, it was found that the distribution ratio increased with decreasing metal concentration, at a given concentration of total pyridine in the aqueous phase. However, a correction of that total pyridine concentration for that complexed as a metal pyridine thiocyanate showed that the distribution ratio was independent of the total metal concentration in the extraction system at any given concentration of free pyridine in the aqueous phase. Thus, polynuclear species were

shown to be absent from the organic phase.

In addition, extraction experiments were carried out in the presence of added pyridinium or picolinium chloride. This addition resulted in no significant change in the distribution ratio of the metal but did result in a small reduction in the concentration of complexed pyridine or picoline in the aqueous phase.

Finally, it was demonstrated that the pyridine or picoline thiocyanate extraction system is a potentially-useful system for the analytical separation of various metals.

PART VIII

APPENDICES

Introduction to the Appendices

Most of the analytical and operational procedures used in the present investigation required some development before use. The final procedures are presented separately and completely in the following Appendices, in a form convenient for routine use.

Appendix I

Purification of Reagents

(1) Conductivity Water

Pass distilled water through a 55-cm x 5-cm column of "Amberlite MB-3", a mixed-bed ion-exchange resin. Store the product in a Pyrex glass bottle.

(2) Alcohol-Free Chloroform (17)

Wash reagent-grade chloroform five times with half its volume of water. Store the product in a brown bottle.

(3) Carbon Dioxide-Free, Anhydrous Chloroform

Add 15 g of anhydrous calcium sulphate to 1500 ml of chloroform contained in a 2000-ml distillation flask. Connect the flask to a conventional all-glass fractionation apparatus with an 80-cm Vigreaux column. Protect the interior of this apparatus with a soda-lime tube. Flush the apparatus with nitrogen, then distil the chloroform at the rate of 4-5 ml per minute. Reject the first 100 ml of distillate and collect the next 1000 $\pm$ 10 ml in a nitrogen-filled receiver that contains 9.0 $\pm$ 0.1 ml of absolute ethanol. Store the product in a brown bottle.

(4) Dioxane (19)

Add 20 g of Gooch-crucible asbestos to 1000 ml of dioxane contained in a 2000-ml flask. Shake the mixture mechanically for one hour. Filter the solution through a Buchner funnel. Store the product in a brown bottle.

(5) Pyridine or Picoline

Add 50 g of anhydrous barium oxide (BaO), as a dehydrating agent, to 1000 ml of pyridine or picoline contained in a 2000-ml flask. Allow the mixture to stand in the dark for a few hours, occasionally shaking it. Connect the flask to a conventional all-glass fractionation apparatus with an 80-cm Vigreaux column. Protect the apparatus with a soda-lime tube. Flush the apparatus with nitrogen. Reflux the liquid under an atmosphere of nitrogen for one hour, then distil it under nitrogen at the rate of 2 ml per minute. Collect the centre 500 ml, then store it in the dark.

Appendix II

Determination of Impurities in Pyridine and 2-Picoline by Gas Chromatography

Chromatograph

A gas chromatograph manufactured by Research Specialties Company, and fitted with conventional thermistor detectors. Connect the thermistor bridge to a potentiometric strip-chart recorder having a full-scale sensitivity of 1 mv and a response of one second.

Column

Apply a coating of Apiezon L grease onto Fisher "Columpak" (30-60 mesh) in the weight ratio 1:6 of substrate to solid. Pack this material into a copper tube 6 feet long and 1/4 inch O.D.

Operating Conditions

Column temperature : 70°C.

Detector temperature ; 75°C.

Injection-block temperature : 150°C.

Helium flow rate : 20 ml/min.

Inlet pressure : 60 mm Hg above atmospheric pressure.

Thermistor current : 20 ma.

Sampling device : Hamilton 10-µl syringe.

Sample size and retention times : see Fig. 2, page 20.

Appendix III

Determination of Impurities in 3-Picoline and 4-Picoline by Gas Chromatography

Chromatograph

Same as in Appendix II.

Column

Apply a coating of tris 1,2,3(2-cyano-ethoxy)propane onto Fisher "Chromosorb W" (30-60 mesh) in the weight ratio 3:7 of substrate to solid. Except for this difference in column packing, the column was similar to that described in Appendix II.

Operating Conditions

Column temperature : 98°C.

Detector temperature : 105°C.

Injection-block temperature : 175°C.

Helium flow rate : 80 ml/min.

Inlet pressure : 570 mm of Hg above atmospheric pressure.

Thermistor current : 20 ma.

Sampling device : Hamilton 10-µl syringe.

Sample size and retention times : see Figs. 3 and 4, pages 23 and 25.

Appendix IV

Solvent-Extraction Procedure

Add[1] standard solutions of nickel chloride, potassium thiocyanate and hydrochloric acid (where used), water, and a standard solution of purified pyridine in that order to a dry extraction flask[2], such that the volume of the aqueous solution is 90.00 ± 0.05 ml. Then add 90.00 ± 0.05 ml of chloroform (reagent-grade, unless specified otherwise). Clamp the capped flask in a mechanical shaker[3]. Allow the contents to reach temperature equilibrium in a water-bath[4]. Then lower the cap of the flask momentarily in order to reduce the pressure to 1 atmosphere. Now shake the vessel mechanically in the water-bath until equilibrium is established (equilibrium was established within 10 minutes for all the metal pyridine and picoline thiocyanate extraction systems; a 10-minute period of shaking was therefore used, unless specified otherwise). Then transfer the contents of the flask to a dry separatory funnel[5] which has been immersed in the constant-temperature bath, and allow the phases to separate in the bath over a period of at least 45 minutes. The transfer need not be quantitative, since the two phases are later analysed without dilution. Remove the funnel from the bath, remove its stem protector, and insert an absorbent-cotton filter plug in the stem of the funnel. Draw most of the chloroform phase into a dry, 100-ml volumetric flask. Do not dilute this solution to volume. Reject the remainder of the chloroform phase, and leave the aqueous phase in the funnel. Remove aliquots of both phases for chemical analysis[6].

NOTES:

(1) For extraction systems other than those containing nickel pyridine thiocyanate, add a standard solution of potassium thiocyanate, water, a standard solution of hydrochloric acid (where used), a standard solution of purified pyridine (or a purified picoline) and chloroform (reagent-grade, unless specified otherwise) in that order to the dry extraction flask. Cap the flask, shake it manually for a few seconds, and then allow the phases to separate. Then add the standard solution of metal chloride. The volumes of the reagents added are to be such that the aqueous and chloroform volumes would each be 90.00 $\pm$ 0.05 ml before mixing. Then proceed as directed in the procedure for the extraction and separation.

(2) The extraction flask: a 500-ml conical, Pyrex flask, with a bakelite screw cap containing a Teflon insert. Grind the top of the threaded neck with a carborundum disc and then with very fine diamond sandpaper, until a water-tight seal between the Teflon and the glass is obtained when the cap is screwed on. In addition, make a slight indentation (with an oxy-acetylene torch) in the side of the flask about one-third of the way down, to fit the Burrell shaker clamp. This method of clamping is preferable to clamping the flask at the cap, which could become loosened during mechanical shaking.

(3) Mechanical shaker: a Burrell Wrist-Action Shaker (Model 00).

(4) Water-bath: 24 in x 18 in x 12 in; fitted with a circulating

pump, heater (500-watt, bayonet type), cooling coil, thermoregulator (Precision Micro-Set), and a thermometer (0-50°C, 0.1°C divisions) which, in the present work, was previously calibrated against a standard 0-50°C thermometer obtained from the National Research Laboratories (serial number 57478). An aluminum shield fitted above the bath prevents splashing during the shaking of extraction flasks. With this water bath-shaker combination, 6 extraction flasks may be shaken simultaneously.

(5) The separatory funnel: a 250-ml Squibb-type, Pyrex funnel equipped with a Teflon stopcock and a ground-glass stopper. Shorten the stem of the funnel to about one inch. In order to prevent water in the water-bath from contaminating the stem of the funnel, slip over the stem a short length of rubber tubing closed at one end by a glass plug.

(6) Use the final (equilibrium) phase volumes given in Table IV, page 38 in the calculation of chemical concentrations.

Appendix V

Determination of True Volumes in Extraction Systems

Apparatus

(1) Separatory funnel: as described in Note 5 of Appendix IV.

(2) Dry, 100-ml volumetric flask: tape a narrow strip of graph paper to the neck of each flask in order to cover the volume range of 98-102 ml. Calibrate each flask for several volumes in this range.

Procedure

Measure 100.00 ± 0.05 ml each of water-saturated chloroform* and chloroform*-saturated water into a separatory funnel. Tilt the separatory funnel end for end, at room temperature, about 25 times. Allow the phases to separate. Make as nearly complete a separation as possible, and draw each phase into a volumetric flask. Record the volume of each phase. The difference between 100 ml and the recovered volume of each phase is the sought-for correction. It represents the unavoidable loss in volume in a solvent-extraction operation in which the phase is drawn off. Therefore, in such an operation these volumes should be added to the recovered volumes in order to get the true volumes.

Repeat these measurements for each of the various test solutions.

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* Reagent-grade chloroform was used to prepare these solutions.

Appendix VI

Potentiometric Determination of Pyridine or Picolines in Aqueous Solutions

Apparatus

A Leeds and Northrup pH Indicator (Cat. No. 7664) in conjunction with a Beckman blue-glass electrode and a Beckman calomel (fibre-type) electrode.

Reagents

(1) Hydrochloric acid: 0.1-M and 0.025-M aqueous solutions. Standardize the 0.1-M solution against sodium carbonate (48). Prepare the 0.025-M solution by dilution of the 0.1-M solution.

Procedure

Transfer a 25-ml aliquot of the solution for analysis to a 100-ml beaker. Carry out a conventional potentiometric titration, agitating the solution with a magnetic stirrer. Near the end point, record the pH readings after each small and equal increment of titrant. Calculate the end point by the method of second differences (49). Typical titration curves are shown in Fig. 7, page 44. The accuracy, precision and concentration range of the determination are shown in Table V, page 43.

Appendix VII

Argentimetric Determination of Thiocyanate in Aqueous Solutions

Reagents

(1) Indicator: saturated aqueous solution of ferric ammonium sulphate.

(2) Nitric acid: 6.0 ± 0.2-M aqueous solution.

(3) Silver nitrate: 0.1-M and 0.025-M aqueous solutions. Standardize the 0.1-M solution against sodium chloride, by Fajans' method (28) with dichlorofluorescein as the indicator and about 0.1 g of dextrin as an anticoagulant. Prepare the 0.025-M solution by dilution of the 0.1-M solution.

(4) Potassium thiocyanate: 0.1-M and 0.025-M aqueous solutions. Standardize the 0.1-M solution against the standard 0.1-M silver nitrate solution, by the Volhard method (28). Prepare the 0.025-M solution by dilution of the 0.1-M solution.

Procedure (28)

Transfer a 25-ml aliquot of the solution for analysis to a 250-ml iodine flask. Add an excess of standard silver nitrate solution and

5 ± 0.5 ml of 6.0-M nitric acid over that required to neutralize the pyridine or picoline. Add 2.0 ± 0.2 ml of the indicator solution, and titrate with the standard thiocyanate solution to the appearance of a brownish tinge which is permanent on strong shaking. Calculate the thiocyanate content* of the sample by difference. The accuracy, precision, and concentration range of the determination are shown in Table VIII, page 50.

* The aqueous phase of a metal pyridine (or picoline) thiocyanate extraction system has a known chloride concentration as well as thiocyanate. By correcting for the chloride, which is not extracted into chloroform, the aqueous thiocyanate concentration is then calculated.

Appendix VIII

Potentiometric Determination of Pyridine or Picolines in Chloroform Solutions

Apparatus

As in Appendix VI. As a precaution, soak the electrodes overnight in water, after use in chloroform.

Reagents

(1) Perchloric acid: 0.025-M in purified dioxane (see Appendix I). Standardize the solution potentiometrically against potassium acid phthalate, as described by Seaman and Allen (51).

Procedure

Transfer an aliquot of the solution for analysis to a 100-ml beaker, and dilute it to 30 ± 5 ml with reagent-grade chloroform. Carry out a conventional potentiometric titration, agitating the solution with a magnetic stirrer. Near the end point, record the millivolt readings after each small and equal increment of titrant. Calculate the end point by the method of second differences (49). Typical titration curves are shown in Fig. 8, page 54. The accuracy, precision and concentration range of the determination are shown in Table IX, page 53.

NOTE:

The presence of a nickel pyridine thiocyanate complex in the chloroform solution of pyridine reduces both the accuracy and the precision of the determination (see Part V-3 for details). The accuracy and precision were not tested in the presence of other metal pyridine thiocyanates, nor was the accuracy and precision of the picoline titration tested in the presence of a metal picoline thiocyanate; it was expected that these complexes, too, would reduce both the accuracy and the precision of the method.

Appendix IX

Argentimetric Determination of Thiocyanate in Chloroform Solutions

Reagents

As in Appendix VII.

Procedure

Transfer a 25-ml aliquot of the solution for analysis to a 100-ml beaker covered with a "Speedyvap" watch glass. Allow the solution to evaporate to dryness in a fume hood, at room temperature; with a good draft, this requires approximately 1 hour. Dissolve* the residue in 25 ± 5 ml of water and quantitatively transfer the solution to a 250-ml iodine flask. Then proceed as in Appendix VII. The validity of this procedure is confirmed by the results in Part IV-4. The accuracy, precision and concentration range of this determination, as for aqueous solutions of thiocyanate, are shown in Table VIII, page 50.

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* If complete dissolution of the residue does not occur at this point then add, in order, an excess of standard silver nitrate solution and 5.0 ± 0.5 ml of 6.0-M nitric acid. Stir the mixture for a few minutes and transfer it quantitatively to a 250-ml iodine flask. Now proceed as in Appendix VII, but omit the addition of silver nitrate and nitric acid.

Appendix X

Potentiometric Determination of Pyridinium or Picolinium Chloride in Aqueous Solutions

Apparatus

As in Appendix VI.

Reagents

(1) Hydrochloric acid: As in Appendix VI.

(2) Sodium hydroxide: 0.1-M and 0.025-M aqueous solutions. Prepare 0.1-M and 0.025-M carbonate-free solutions from a 50 percent solution as described by Day and Underwood (48). Standardize them potentiometrically as described below against an aliquot of standard 0.1-M or 0.025-M hydrochloric acid. Store these alkali solutions in polyethylene bottles protected with soda-lime tubes.

Procedure

Transfer an aliquot of the solution for analysis to a 100-ml beaker. Carry out a conventional potentiometric titration with the 0.1-M or 0.025-M standard solution of alkali, agitating the solution with a magnetic stirrer. Near the end point, record the pH readings after each small and equal increment of titrant. Calculate the end point

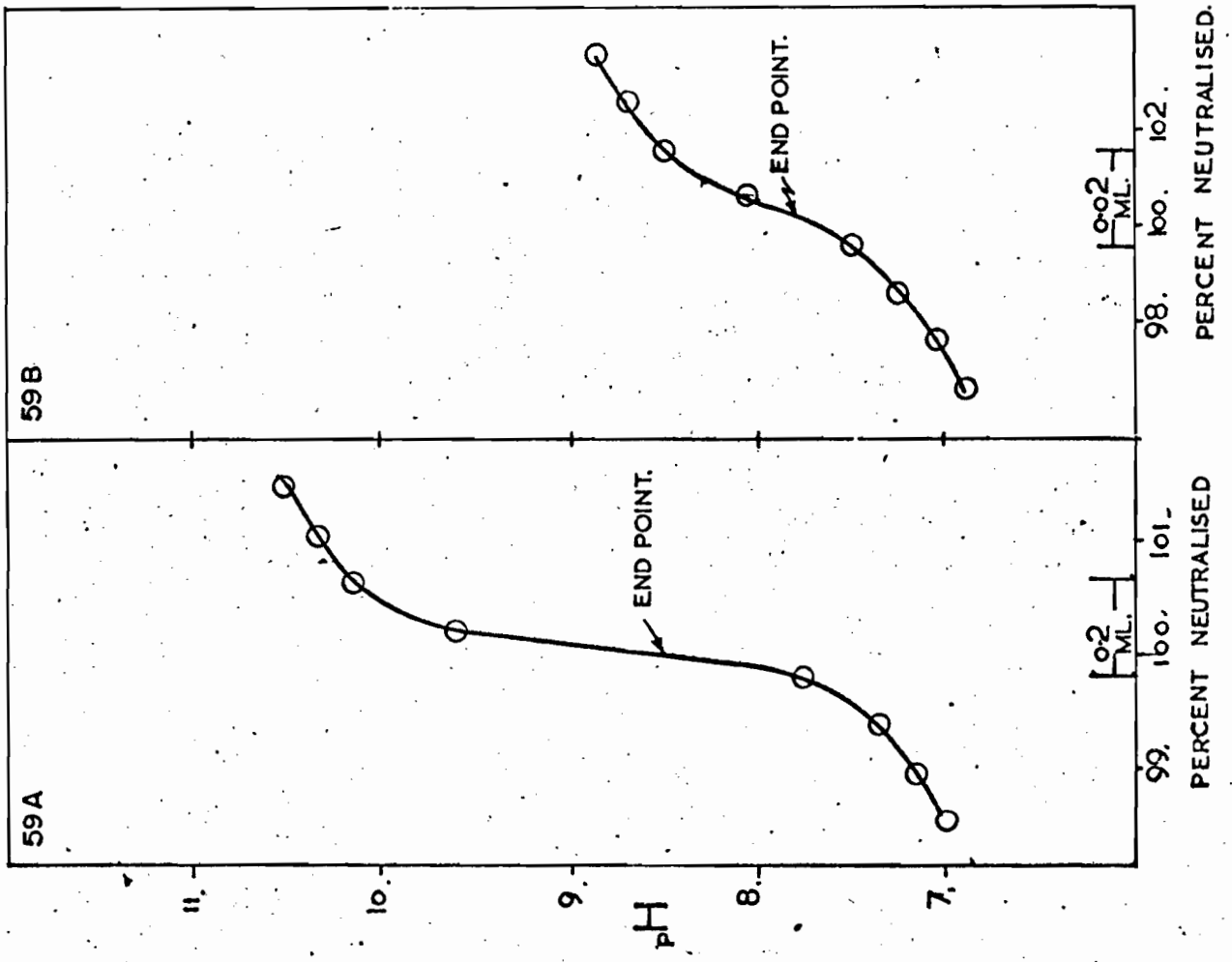
by the method of second differences (49). Typical titration curves are shown in Fig. 59. The accuracy, precision and concentration range of this determination, in the presence of a known amount of pyridine, are shown in Table VI, page 47.

FIGURE 59

Typical potentiometric titration curves for the determination of pyridinium chloride in aqueous solutions.

(A) 0.05-M pyridinium chloride vs 0.1-M, carbonate-free sodium hydroxide.

(B) 0.001-M pyridinium chloride vs 0.025-M, carbonate-free sodium hydroxide.


59 A
59 B
END POINT.
END POINT.
pH
11.
10.
9.
8.
7.
.02 ML.
.02 ML.
99.
100.
101.
98.
100.
102.
PERCENT NEUTRALISED
PERCENT NEUTRALISED.

Appendix XI

Determination of Nickel by Titration with Ethylenediaminetetraacetic Acid

Reagents

(1) Ammonium hydroxide: 7.0 ± 0.2-M aqueous solution.

(2) Indicator: grind 0.20 ± 0.01 g of Murexide with 100 g of sodium chloride.

(3) Ethylenediaminetetraacetic acid, disodium salt (EDTA): 0.01-M aqueous solution. Standardize this solution against calcium carbonate as described by Harris and Sweet (38).

(A) Procedure for Aqueous Solutions (38)

Add 5.0 ± 0.2 ml of 7.0-M ammonium hydroxide to 50 ml of the neutral or slightly acidic solution containing up to 30 mg of nickel. Add 200 ± 20 mg of the Murexide indicator powder, then titrate the solution with the 0.01-M standard solution of EDTA. The end point is a change in color from yellow to purple, the end point being taken as the disappearance of the last perceptible tinge of yellow (the last perceptible darkening of the solution to purple). The accuracy, precision and concentration range of the determination are shown in Table X, page 59.

(B) Procedure for Chloroform Solutions

Transfer an aliquot of the chloroform solution for analysis, containing up to 30 mg of nickel, to a 100-ml beaker. Cover the beaker with a "Speedyvap" watch glass. Allow the solution to evaporate to dryness in a fume hood, at room temperature; with a good draft, this requires approximately 1 hour. Dissolve the residue in 50 ml of water containing a few drops of 15.7-M nitric acid. Then follow exactly the entire procedure given above for aqueous solutions. The validity of this procedure is shown by the results in Part IV-5-1. The accuracy, precision and concentration range of this determination, as for aqueous solutions of nickel, are shown in Table X, page 59.

Appendix XII

Colorimetric Determination of Nickel

Apparatus

A Unicam SP 1400 Prism Absorptiometer with a conventional 1-inch cylindrical absorption cell.

Reagents

1) Dimethylglyoxime: 1.0 ± 0.1 percent in absolute ethanol. The solution is stable.

2) Citric acid: 10.0 ± 0.2 percent aqueous solution.

3) Potassium persulphate: 2.0 ± 0.1 percent aqueous solution.

4) Sodium hydroxide: 2.0 ± 0.1-M aqueous solution.

5) Hydrochloric acid: 1.0 ± 0.1-M aqueous solution.

6) Nickel standard: 10 µg of nickel per ml of aqueous solution. Prepare this solution by volumetric dilution of a 0.05-M nickel chloride stock solution. Standardize this stock solution against a 0.01-M solution of EDTA, which has previously been standardized according to Procedure A of Appendix XI.

Procedure (34)

Transfer an aliquot of the thiocyanate-free solution[1] containing between 0 and 300 μg of nickel to a 100-ml volumetric flask. Add 10.00 ± 0.02 ml of 1-M hydrochloric acid, and dilute the solution to 50 ± 5 ml. Add 1.00 ± 0.01 ml of 10 percent citric acid, 3.00 ± 0.01 ml of 2 percent potassium persulphate, 15.00 ± 0.02 ml of 2.0-M sodium hydroxide, and 1.00 ± 0.01 ml of 1 percent dimethylglyoxime in ethanol. Then heat the solution to 60°C, and maintain it at 60-70°C for 5 minutes. Cool it to room temperature and dilute to volume. Measure the absorbance[2] at 465 mμ and subtract the absorbance value obtained with a reagent blank, with water as the spectrophotometric blank in both cases. Calculate the nickel concentration of the sample from a previously prepared calibration curve[3]. Beer's Law is obeyed.

NOTES:

(1) Thiocyanate causes rapid color fading, and therefore it should be absent. It may be removed by the procedure recorded in Appendix XIII. See then Note (3) below.

(2) Color development will be complete by the time the solution has cooled to room temperature either in air or in an ice bath. Thereafter, the color is stable for at least 24 hours.

(3) At 465 mμ a solution containing 1.50 μg of nickel per ml of

solution gave an absorbance of 0.82 in the 1-inch cell. When the colorimetric procedure is preceded by the procedure in Appendix XIII, then an identical solution gave an absorbance of 0.79 in the 1-inch cell. The absorbance of the reagent blank of each experiment was identical; its value (0.002 compared to water) was subtracted from the absorbance of each sample to give the values reported above.

Appendix XIII

Elimination of Thiocyanate From an Aqueous or Chloroform Solution Containing Pyridine or Picoline

CAUTION: In the Procedure, hydrogen cyanide gas is produced. Carry out all operations in a fume hood with a good draft.

Reagents

(1) **Nitric acid:** 6.0 ± 0.2-M aqueous solution.

Procedure

Transfer 50 ml or less of the solution to a 100-ml beaker covered with a "Speedyvap" watch glass. Place the beaker in a fume hood with a good draft. Allow chloroform solutions to evaporate to dryness at room temperature; this requires approximately 1 hour. Evaporate aqueous solutions to 4 or 5 ml on a hot plate; this requires approximately 30 minutes. Then allow the beaker to cool. Rinse the beaker and watch glass with 15 ± 3 ml of 6.0-M nitric acid, then allow the solution to stand in the cold, in the fume hood, until any reaction has ceased. Then evaporate the solution to 4 or 5 ml on a hot plate. By using 15 ml more of the 6.0-M nitric acid, repeat the rinsing and evaporation steps, then finally evaporate the solution to dryness on a steam bath. Dissolve the residue in 20 ± 5 ml of water.

NOTE:

The oxidation of thiocyanate by nitric acid is by a complicated route. At room temperature the solution slowly turns brown if enough thiocyanate is present. The reaction is strongly exothermic. The reaction rate will suddenly become great. Hydrogen cyanide is evolved rapidly, and the solution quickly becomes clear. The dissolved hydrogen cyanide is then boiled out.

Appendix XIV

Colorimetric Determination of Cobalt

CAUTION: If thiocyanate is present in the sample then, during the treatment with nitric acid in the Procedure, hydrogen cyanide will be evolved. It is therefore advisable to remove the thiocyanate from the sample, by the procedure recorded in Appendix XIII, before beginning the following colorimetric analysis.

Apparatus

1) A Unicam SP 1400 Prism Absorptiometer with a conventional 1-inch cylindrical absorption cell.

2) A pH meter with a glass-calomel electrode pair.

Reagents

1) Sodium acetate: crystalline hydrate ($CH_3COONa \cdot 3H_2O$).

2) Hydrochloric acid: 1.0-M aqueous solution.

3) Sodium hydroxide: 1.0-M aqueous solution.

4) Nitroso-R salt: 0.2 percent aqueous solution.

5) Nitric acid: 15.7-M aqueous solution.

6) Cobalt standard: 10 μg of cobalt per ml of aqueous solution. Prepare this cobalt solution by volumetric dilution of a 0.02-M cobalt chloride solution which has been accurately standardized by a conventional EDTA titration, using Murexide as indicator (39).

Procedure

Transfer 25 ml or less of the thiocyanate-free solution[1], containing between 0 and 350 μg of cobalt, to a 100-ml beaker. Add 4.0 ± 0.2 g of solid sodium acetate and then, by using a pH meter, adjust the pH to 5.5 ± 0.1 either with 1.0-M hydrochloric acid or with 1.0-M sodium hydroxide solution. Transfer the solution quantitatively to a 100-ml Pyrex volumetric flask. Add 5.00 ± 0.01 ml of the 0.2 percent aqueous solution of Nitroso-R salt. Boil the solution for 2 minutes on a hot plate, adding 4.0 ± 0.1 ml of 15.7-M nitric acid dropwise to the solution after the first minute. Cool the solution in the dark, then dilute it to volume. Measure the absorbance[2] at 550 mμ against water, and correct the result for a reagent blank read against water (the reagent blank in the present investigation had an absorbance of 0.001 compared to water).

Calculate the cobalt concentration of the sample from a previously prepared calibration curve. Read the standard solution and

the reagent blank against water (the spectrophotometric blank). Beer's Law is obeyed.

NOTES:

(1) The presence of more than 0.0002 mole of thiocyanate will likely cause a positive error in the absorbance, and therefore it should be absent. Thiocyanate may be removed by the procedure in Appendix XIII.

In one test a thiocyanate-free solution containing 2.15 μg of cobalt per ml of solution gave an absorbance of 0.82 at 550 mμ in the 1-inch cell. The same absorbance value was also obtained when an identical sample was treated first by the procedure in Appendix XIII, then by the present procedure. However, when the initial sample contained 0.007 mole of thiocyanate, and the procedure in Appendix XIII was carried out, then a solution containing 2.15 μg of cobalt per ml of solution gave an absorbance of 0.85 in the 1-inch cell. The three samples and their respective reagent blanks were read against water. Each reagent blank had an absorbance of 0.002 compared to water.

(2) Color development will be complete by the time the solution has cooled to room temperature; thereafter, the color is stable for at least 12 hours if kept in the dark.

Appendix XV

Determination of Zinc or Cadmium by Titration with Ethylenediaminetetraacetic Acid

Reagents

(1) Buffer solution: 2.0-M ammonium chloride solution mixed with an equal volume of 2.0-M ammonium hydroxide solution. The pH should be approximately ten.

(2) Indicator: 0.20 g of Eriochrome Black T dissolved in 10 ± 2 ml of the above buffer and diluted to 100 ml with water.

(3) Ethylenediaminetetraacetic acid, disodium salt (EDTA): 0.01-M aqueous solution. Standardize this solution against pure zinc (82).

(A) Procedure for Aqueous Solutions (44)

Transfer a 50-ml aliquot of the solution containing up to 30 mg of zinc or 50 mg of cadmium to a 100-ml beaker. Neutralize the solution, and then add 5.0 ± 0.5 ml of the buffer solution. Add a few drops of the indicator solution, and titrate with the 0.01-M standard solution of EDTA until the color changes from wine-red to blue. The end point is taken as the disappearance of the last perceptible tinge of red (the last perceptible darkening of the solution to purple). The accuracy, precision and concentration range of this determination are shown in Table XIII, page 71.

(B) Procedure for Chloroform Solutions

Transfer an aliquot of the chloroform solution for analysis, containing up to 30 mg of cadmium or zinc, to a 100-ml beaker. Cover the beaker with a "Speedyvap" watch glass. Allow the solution to evaporate to dryness in a fume hood, at room temperature; with a good draft, this requires approximately 1 hour. Dissolve the residue in 50 ml of water containing a few drops of 12.0-M hydrochloric acid. Then follow exactly the entire procedure given above for aqueous solutions. The accuracy, precision and concentration range of this determination, as for aqueous solutions of zinc or cadmium, are shown in Table XIII, page 71.

Appendix XVI

Computed Data for the Metal Pyridine and Picoline Thiocyanate Extraction Systems

1. Introduction

The purpose of the present Appendix was to list data which were needed in Part VI, and to describe, where necessary, the methods used to obtain the data.

The computed values of $[P]$, the concentration of free pyridine (or picoline) in the aqueous phase, and of p*, the apparent partition coefficient of pyridine (or picoline) in the metal pyridine and picoline thiocyanate extraction systems are in Tables LXXIII to XCVIII, together with the basic experimental data for each extraction experiment. Also given are the values for log $[P]$, log D (the logarithm of the distribution ratio of the metal), and p_t, another form of pyridine or picoline partition coefficient which was needed for the calculations described below.

The method of calculation of p* has been described in Part VI-1. The values of p_t were read from Figs. 25 to 46.

However, to find $[P]$, it was first necessary to find p**, the extrapolated value of p* at zero concentration of pyridine or picoline. Then K', a constant defined by equation (36) was found. Finally $[P]$ was found from equation (37). The calculation of $[P]$ has been described in Part VI-2.

The methods used to obtain the best values of p** and K' together with their 95 percent confidence limits are described below.

TABLES LXXIII TO XCVIII

Computed data for the metal pyridine and picoline thiocyanate extraction systems.

LEGEND:

$[P]_{T,o}$ = Total concentration of pyridine (or picoline) in the organic phase.

$[M]_{T,o}$ = Total concentration of metal in the organic phase.

$[P]_{T,A}$ = Total concentration of pyridine (or picoline) in the aqueous phase.

p^* = The apparent partition coefficient of pyridine (or picoline) in the presence of a metal pyridine or picoline thiocyanate; see equation (23) for a formal definition.

$[M]_{T,A}$ = Total concentration of metal in the aqueous phase.

$[P]$ = Concentration of free pyridine (or picoline) in the aqueous phase; $[P]$ is calculated from equation (37).

p_t = A form of pyridine (or picoline) partition coefficient defined by equation (39); the values listed were read from Figs. 25 to 36.

log D = Logarithm of the distribution ratio of the metal; D is defined by equation (1).

NOTES:

(1) Reference to other computed data for each solvent-extraction system are given in the Tables below.

(2) The data in the Tables are for equilibrated solvent-extraction systems at 25.0°C. The aqueous phase for each system was 0.3 M in potassium thiocyanate.

(3) All concentrations are molar concentrations.

(4) The metal concentration specified in each Table heading is the value initially present in the aqueous phase, before equilibration.

(5) The value of K' used to obtain $[P]$ from equation (37) is noted in each Table; when K = 0, $[P] = [P]_{T,A}$

TABLE LXXIII

Cobalt pyridine thiocyanate (0.0025 M); extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log[P]	log D
1	0	0	0	-	2.58	14.1	0	-	-
2	13.1	0.0142	1.02	12.8	2.55	14.1	0.964	-3.015	-2.254
3	26.3	0.208	1.84	13.8	2.38	14.2	1.75	-2.757	-1.059
4R	39.6	0.709	2.68	13.7	1.89	14.2	2.57	-2.589	-0.426
5	52.6	1.32	3.48	13.6	1.28	14.3	3.39	-2.470	0.013
6	65.9	1.85	4.17	14.0	0.799	14.3	4.10	-2.387	0.364
7	79.0	2.18	4.94	14.2	0.461	14.3	4.89	-2.310	0.675
8	92.1	2.37	5.76	14.3	0.272	14.3	5.73	-2.242	0.941
9	105.	2.48	6.64	14.3	0.169	14.3	6.62	-2.179	1.167
10	156.	2.60	10.3	14.1	0.0370	14.3	10.3	-1.987	1.846

NOTES: (1) Basic data are in Table XL.

(2) Extraction 4R is the mean of 4 replicates.

(3) $K' = 23.3$

TABLE LXXIV

Cobalt pyridine thiocyanate (0.0025 M); pyridinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	2.58	14.1	0	-	-
2	13.1	0.0145	0.966	13.5	2.44	14.2	0.940	-3.026	-2.226
3	26.1	0.212	1.86	13.6	2.37	14.2	1.81	-2.741	-1.048
4	39.5	0.709	2.57	14.3	1.90	14.3	2.52	-2.599	-0.428
5	52.6	1.33	3.34	14.2	1.29	14.3	3.29	-2.482	0.013
6	66.0	1.83	4.04	14.5	0.810	14.4	4.00	-2.397	0.354
7	79.1	2.18	4.83	14.6	0.466	14.4	4.80	-2.318	0.670
8	105.	2.48	6.75	14.1	0.168	14.4	6.74	-2.171	1.170
9	156.	2.60	10.2	14.3	0.0357	14.4	10.2	-1.991	1.862

NOTES: (1) Basic data are in Table XLII.

(2) $K' = 11.3$.

TABLE LXXV

Cobalt pyridine thiocyanate (0.0005 M); extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	13.1	0.00272	0.941	13.9	0.517	14.1	0.930	-3.031	-2.278
2	26.3	0.0435	1.84	14.2	0.475	14.2	1.82	-2.739	-1.038
3	39.3	0.163	2.75	14.1	0.363	14.2	2.73	-2.564	-0.348
4	52.4	0.309	3.60	14.2	0.225	14.3	3.58	-2.445	0.137
5	65.4	0.406	4.55	14.0	0.122	14.3	4.54	-2.343	0.522
6	78.7	0.464	5.26	14.6	0.0689	14.3	5.25	-2.279	0.828
7	91.6	0.490	6.22	14.4	0.0403	14.3	6.21	-2.206	1.086
8	104.	0.503	7.00	14.6	0.0257	14.3	7.00	-2.155	1.292

NOTES: (1) Basic data are in Table XLI.

(2) $K' = 23.3$

TABLE LXXVI

Cobalt pyridine thiocyanate (0.0005 M); pyridinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	12.9	0.00286	0.879	14.6	0.518	14.2	0.874	-3.058	-2.258
2	26.1	0.0459	1.82	14.2	0.499	14.2	1.81	-2.742	-1.036
3	39.2	0.166	2.71	14.2	0.361	14.3	2.70	-2.568	-0.337
4	52.4	0.310	3.54	14.5	0.222	14.4	3.53	-2.452	0.146
5	65.4	0.408	4.43	14.4	0.121	14.4	4.42	-2.355	0.528
6	78.5	0.461	5.26	14.6	0.0676	14.4	5.26	-2.279	0.834

NOTES: (1) Basic data are in Table XLIII.

(2) $K' = 11.3$

TABLE LXXVII

Cobalt 2-picoline thiocyanate (0.0025 M); extraction into chloroform

Ext. No.	$[P]_{T,A} \times 10^3$	$\log [P]_{T,A}$	log D
1	0	-	-
2	3.82	-2.418	-1.807
3R	9.39	-2.027	-1.099
4	12.9	-1.889	-0.804
5	19.8	-1.703	-0.444
6	26.3	-1.580	-0.190
7	34.3	-1.465	0.029
8	41.6	-1.381	0.173
9	51.6	-1.287	0.348
10	59.1	-1.228	0.444
11	78.4	-1.106	0.654
12	130.	-0.886	1.079
13	476.	-0.332	1.534

NOTES: (1) Basic data are in Table XLVIII.
(2) Extraction 3R is the mean of 4 replicates.
(3) K' was not found for this system.

TABLE LXXVIII

Cobalt 3-picoline thiocyanate (0.0025 M); extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10$	$[M]_{T,o} \times 10$	$[P]_{T,A} \times 10$	p*	$[M]_{T,A} \times 10$	p_t	$[P] \times 10$	log [P]	log D
1	0	0	0	-	2.57	54.7	0	-	-
2	14.2	0.0325	0.315	44.7	2.54	54.7	0.278	-3.555	-1.893
3	27.4	0.326	0.542	48.1	2.26	54.7	0.489	-3.313	-0.842
4	38.4	0.755	0.722	49.0	1.84	54.7	0.660	-3.180	-0.387
5	48.3	1.22	0.873	49.7	1.39	54.7	0.816	-3.088	-0.057
6R	56.9	1.58	0.914	55.3	1.03	54.7	0.869	-3.060	0.185
7	71.0	2.06	1.20	52.3	0.582	54.7	1.17	-2.933	0.549
8	85.2	2.30	1.34	56.7	0.315	54.7	1.32	-2.879	0.864
9	100.	2.46	1.66	54.3	0.176	54.7	1.65	-2.783	1.146
10	113.	2.54	1.97	52.2	0.103	54.7	1.96	-2.707	1.393
11	155.	2.60	2.72	53.2	0.030	54.7	2.72	-2.566	1.938

NOTES: (1) Basic data are in Table XLIX.

(2) Extraction 6R is the mean of 4 replicates.

(3) $K' = 52.4$.

TABLE LXXIX

Cobalt 3-picoline thiocyanate (0.0025 M); picolinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	2.57	57.2	0	-	-
2	14.2	0.0332	0.278	50.6	2.54	57.2	0.246	-3.608	-1.883
3	28.4	0.381	0.524	51.3	2.20	57.2	0.472	-3.326	-0.762
4	39.0	0.761	0.672	53.5	1.84	57.2	0.615	-3.210	-0.384
5	47.9	1.23	0.808	53.2	1.38	57.2	0.756	-3.121	-0.050
6	56.9	1.59	0.899	56.2	1.02	57.2	0.856	-3.067	0.193
7	71.1	2.05	1.16	54.2	0.582	57.2	1.13	-2.947	0.547
8	98.9	2.46	1.69	52.7	0.178	57.2	1.68	-2.775	1.140

NOTES: (1) Basic data are in Table L.

(2) $K' = 51.6$.

TABLE LXXX

Cobalt 4-picoline thiocyanate (0.0025 M); extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	2.58	47.2	0	-	-
2	11.1	0.0521	0.228	47.8	2.52	47.2	0.204	-3.691	-1.684
3	17.0	0.380	0.372	41.6	2.22	47.2	0.337	-3.472	-0.767
4	22.7	0.777	0.471	41.6	1.83	47.2	0.434	-3.362	-0.372
5	28.4	1.22	0.552	42.6	1.40	47.2	0.518	-3.285	-0.060
6R	34.1	1.59	0.619	44.8	1.02	47.2	0.591	-3.228	0.193
7	42.0	2.05	0.748	45.2	0.596	47.2	0.728	-3.137	0.537
8	51.0	2.34	0.915	45.5	0.310	47.2	0.902	-3.044	0.879
9	58.9	2.49	1.06	46.2	0.168	47.2	1.05	-2.978	1.170
10	68.0	2.53	1.22	47.4	0.0955	47.2	1.21	-2.915	1.423
11	124.	2.63	2.40	47.3	0.00805	47.2	2.40	-2.619	2.515

NOTES: (1) Basic data are in Table LI.

(2) Extraction 6R is the mean of 4 replicates.

(3) $K' = 48.1$.

TABLE LXXXI

Cobalt 4-picoline thiocyanate (0.0025 M); picolinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	P_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	2.57	49.6	0	-	-
2	9.09	0.0535	0.184	48.2	2.53	49.6	0.178	-3.749	-1.674
3	17.1	0.394	0.308	50.4	2.20	49.6	0.299	-3.524	-0.747
4	22.7	0.787	0.437	44.7	1.82	49.6	0.427	-3.370	-0.365
5	28.4	1.21	0.492	47.9	1.41	49.6	0.483	-3.316	-0.067
6	34.2	1.56	0.580	48.2	1.06	49.6	0.572	-3.242	0.167
7	42.0	2.05	0.670	50.5	0.594	49.6	0.665	-3.177	0.538
8	58.9	2.48	1.02	48.0	0.173	49.6	1.02	-2.992	1.155

NOTES: (1) Basic data are in Table LII.

(2) $K' = 13.0$.

TABLE LXXXII

Nickel pyridine thiocyanate (0.005 M); extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	5.12	14.1	0	-	-
2	1.05	0.00143	0.187	5.58	5.14	14.2	0.113	-3.946	-3.556
3	5.55	0.143	0.469	10.6	4.98	14.3	0.290	-3.538	-1.542
4	10.6	0.818	0.716	10.2	4.34	14.4	0.469	-3.329	-0.726
5	16.7	1.71	0.870	11.3	3.47	14.5	0.615	-3.211	-0.307
6	22.4	2.70	0.953	12.2	2.59	14.5	0.730	-3.136	0.017
7	28.1	3.59	1.08	12.7	1.64	14.6	0.980	-3.041	0.340
8R	34.0	4.30	1.27	13.3	0.977	14.6	1.14	-2.941	0.643
9	39.3	4.78	1.58	12.8	0.518	14.7	1.50	-2.825	0.965
10	45.0	5.06	1.82	13.6	0.264	14.8	1.77	-2.751	1.283
11	49.9	5.20	2.24	13.0	0.139	14.9	2.21	-2.655	1.573
12	62.0	5.27	2.69	15.2	0.0474	14.9	2.68	-2.572	2.045
13	111.	5.32	6.04	14.8	0.00983	14.9	6.04	-2.219	2.734

NOTES: (1) Basic data are in Table XXIX.
(2) Extraction 8R is the mean of 5 replicates.
(3) K' = 129.

TABLE LXXXIII

Nickel pyridine thiocyanate (0.005 M); pyridinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	5.11	14.1	0	-	-
2	5.57	0.152	0.432	11.5	4.96	14.3	0.352	-3.453	-1.513
3	11.1	0.814	0.649	12.1	4.36	14.4	0.542	-3.265	-0.728
4	16.8	1.66	0.755	13.5	3.48	14.4	0.653	-3.185	-0.321
5	22.4	2.65	0.924	12.8	2.60	14.5	0.828	-3.081	0.008
6	28.0	3.50	1.15	12.2	1.75	14.6	1.07	-2.971	0.301
7	33.8	4.22	1.26	13.4	0.955	14.6	1.21	-2.917	0.645
8	39.5	4.72	1.40	14.7	0.538	14.7	1.37	-2.863	0.943
9	45.0	5.02	1.68	14.8	0.252	14.8	1.66	-2.779	1.299

NOTES: (1) Basic data are in Table XXXII.

(2) $K' = 46.3$.

TABLE LXXXIV

Nickel pyridine thiocyanate (0.0025 M); extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	5.56	0.0927	0.442	11.7	2.46	14.2	0.339	-3.469	-1.424
2	8.15	0.297	0.620	11.2	2.24	14.2	0.487	-3.312	-0.876
3	10.1	0.594	0.707	10.9	1.97	14.2	0.572	-3.242	-0.520
4	16.6	1.27	0.919	12.5	1.28	14.3	0.799	-3.097	-0.003
5	22.3	1.86	1.14	13.1	0.729	14.3	1.05	-2.977	0.407
6	27.9	2.22	1.40	13.6	0.345	14.4	1.35	-2.870	0.809
7	33.3	2.44	1.70	13.8	0.163	14.4	1.67	-2.777	1.176
8	44.3	2.59	2.35	14.4	0.0430	14.5	2.34	-2.630	1.780

NOTES: (1) Basic data are in Table XXX.

(2) K' = 129.

TABLE LXXXV

Nickel pyridine thiocyanate (0.0005 M); extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	5.57	0.0223	0.437	12.7	0.482	14.2	0.413	-3.384	-1.334
2	8.17	0.0877	0.603	13.0	0.428	14.2	0.574	-3.241	-0.690
3	10.9	0.199	0.767	13.2	0.318	14.2	0.739	-3.131	-0.203
4	13.7	0.288	0.954	13.1	0.232	14.2	0.929	-3.031	0.093
5	16.4	0.384	1.11	13.4	0.140	14.3	1.09	-2.961	0.438
6	22.0	0.478	1.40	14.3	0.0552	14.3	1.39	-2.856	0.938
7	32.9	0.516	2.13	14.5	0.0107	14.4	2.13	-2.672	1.683
8	38.4	0.527	2.52	14.4	0.00596	14.4	2.52	-2.598	1.946
9	43.8	0.525	2.89	14.4	0.00413	14.4	2.89	-2.539	2.104
10	49.2	0.528	3.20	14.7	0.00245	14.4	3.20	-2.494	2.332
11	60.0	0.530	4.19	13.8	0.00155	14.4	4.19	-2.377	2.534

NOTES: (1) Basic data are in Table XXXI.

(2) K' = 129.

TABLE LXXXVI

Nickel pyridine thiocyanate (0.0025 M); extraction into benzene

Ext. No.	$[P]_{T,A} \times 10^3$	$[M]_{T,A} \times 10^3$	$[P] \times 10^3$	log [P]	log D
2	1.46	2.43	1.15	-2.940	-1.202
3	2.27	1.82	1.91	-2.718	-0.371
4	2.85	1.03	2.59	-2.586	0.179
1	2.28	1.82	1.92	-2.716	-0.374

NOTES: (1) Basic data for extractions 2, 3 and 4 are in Table XXXIV.

(2) Basic data for extraction 1 are in Table XXXV.

(3) Extraction 3 is the mean of 3 replicates.

(4) Extraction 1 is the mean of duplicates.

(5) K' = 129.

TABLE LXXXVII

Nickel pyridine thiocyanate (0.0025 M); pyridinium chloride added; extraction into benzene

Ext. No.	$[P]_{T,A} \times 10^3$	$[M]_{T,A} \times 10^3$	$[P] \times 10^3$	log [P]	log D
5	1.41	2.43	1.27	-2.894	-1.186
6	2.16	1.82	2.00	-2.697	-0.373
7	2.78	1.03	2.67	-2.574	0.179
3	2.18	1.81	2.02	-2.693	-0.365

NOTES: (1) Basic data for extractions 5, 6 and 7 are in Table XXXIV.

(2) Basic data for extraction 3 are in Table XXXV.

(3) Extraction 3 is the mean of duplicates.

(4) $K' = 46.3$.

TABLE LXXXVIII

Nickel pyridine thiocyanate (0.0005 M); extraction into benzene

Ext. No.	$[P]_{T,A} \times 10^3$	$[M]_{T,A} \times 10^3$	$[P] \times 10$	log [P]	log D
8	1.46	0.469	1.39	-2.857	-0.979
9	2.59	0.242	2.53	-2.596	0.057
10	3.71	0.0786	3.68	-2.433	0.748
5	2.00	0.373	1.92	-2.715	-0.408

NOTES: (1) Basic data for extractions 8, 9 and 10 are in Table XXXIV.

(2) Basic data for extraction 5 are in Table XXXV.

(3) Extraction 5 is the mean of duplicates.

(4) $K' = 129$.

TABLE LXXXIX

Nickel 3-picoline thiocyanate (0.005 M); picolinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	5.12	57.2	0	-	-
2	5.58	0.219	0.102	46.1	4.91	57.2	0.0775	-4.110	-1.351
3	11.4	1.00	0.154	48.1	4.15	57.2	0.122	-3.914	-0.618
4	17.1	1.92	0.230	41.0	3.27	57.2	0.190	-3.720	-0.231
5	22.9	2.69	0.273	44.5	2.53	57.2	0.235	-3.628	0.025
6	28.7	3.69	0.287	48.6	1.56	57.2	0.261	-3.583	0.373
7	34.4	4.36	0.327	51.9	0.907	57.2	0.309	-3.509	0.682
8	45.8	5.06	0.430	59.4	0.229	57.2	0.424	-3.372	1.344
9	57.1	5.22	0.642	56.4	0.0695	57.2	0.639	-3.194	1.876

NOTES: (1) Basic data are in Table LIII.

(2) $K' = 64.6$.

TABLE XC

Nickel 4-picoline thiocyanate (0.005 M); picolinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	5.12	49.6	0	-	-
2	5.70	0.638	0.0992	31.7	4.50	49.6	0.0689	-4.161	-0.847
3	11.5	1.55	0.133	39.8	3.63	49.6	0.0983	-4.007	-0.370
4	17.2	2.74	0.147	42.4	2.48	49.6	0.118	-3.926	0.041
5	23.0	3.81	0.178	43.6	1.45	49.6	0.156	-3.806	0.420
6	2877	4.67	0.229	43.8	0.612	49.6	0.216	-3.665	0.883
7	34.4	5.11	0.276	50.6	0.191	49.6	0.271	-3.566	1.428
8	45.8	5.26	0.466	53.1	0.0280	49.6	0.465	-3.332	2.274
9	57.0	5.29	0.710	50.5	0.0163	49.6	0.709	-3.149	2.512

NOTES: (1) Basic data are in Table LIV.

(2) $K' = 98.3$.

TABLE XCI

Zinc pyridine thiocyanate (0.005 M); extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	5.11	14.1	0	-	-
2	5.39	0.348	0.324	14.5	4.79	14.1	0.307	-3.513	-1.138
3	10.7	1.04	0.653	13.2	4.13	14.2	0.623	-3.205	-0.597
4	16.2	1.82	0.959	13.1	3.35	14.2	0.923	-3.034	-0.264
5	21.6	2.52	1.25	13.2	2.68	14.3	1.21	-2.916	-0.027
6	27.6	3.16	1.45	14.7	2.05	14.3	1.42	-2.848	0.188
7	32.4	3.58	1.80	14.0	1.64	14.4	1.77	-2.752	0.338
8	37.8	3.93	2.13	14.1	1.29	14.4	2.10	-2.678	0.484
9	43.1	4.21	2.41	14.4	1.02	14.4	2.38	-2.623	0.616
10	48.4	4.41	2.76	14.3	0.823	14.4	2.73	-2.563	0.729
11	54.8	4.58	3.19	14.3	0.663	14.4	3.17	-2.499	0.839
12	81.9	4.93	4.94	14.6	0.295	14.4	4.92	-2.307	1.223
13R	108.6	5.06	6.79	14.5	0.172	14.4	6.78	-2.168	1.468
14	135.2	5.12	8.75	14.3	0.108	14.4	8.74	-2.058	1.676

NOTES: (1) Basic data are in Table XLIV.
(2) Extraction 13R is the mean of 4 replicates.
(3) $K' = 11.8$.

TABLE XCII

Zinc pyridine thiocyanate (0.005 M); pyridinium chloride added;
extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	5.10	14.1	0	-	-
2	5.24	0.351	0.348	13.0	4.77	14.3	0.336	-3.473	-1.133
3	10.6	1.04	0.607	14.0	4.12	14.4	0.590	-3.229	-0.597
4	15.9	1.79	0.852	14.5	3.40	14.5	0.832	-3.080	-0.278
5	21.2	2.47	1.11	14.6	2.72	14.6	1.09	-2.963	-0.042
6	31.8	3.54	1.69	14.6	1.67	14.9	1.67	-2.777	0.326
7	42.4	4.18	2.25	15.1	1.06	15.0	2.23	-2.651	0.596
8	53.0	4.53	2.93	15.0	0.700	15.0	2.92	-2.535	0.812
9	79.1	4.94	4.59	15.1	0.321	15.0	4.58	-2.339	1.188
10	105.	5.07	6.26	15.1	0.183	15.0	6.25	-2.203	1.442
11	131.	5.12	7.97	15.1	0.117	15.0	7.96	-2.098	1.641
12	208.	5.15	13.2	15.0	0.0566	15.0	13.2	-1.879	1.959

NOTES: (1) Basic data are in Table XLV.

(2) K_t = 7.2.

TABLE XCIII

Zinc 3-picoline thiocyanate (0.005 M); picolinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	5.10	57.2	0	-	-
2	5.75	1.09	0.060	59.5	4.07	57.2	0.058	-4.238	-0.572
3	11.5	2.44	0.082	80.7	2.74	57.2	0.080	-4.097	-0.050
4	17.2	3.51	0.206	49.4	1.70	57.2	0.203	-3.693	0.314
5	22.9	4.22	0.245	59.0	1.01	57.2	0.243	-3.615	0.621
6	28.6	4.62	0.370	52.3	0.622	57.2	0.368	-3.434	0.871
7	34.3	4.86	0.420	58.5	0.407	57.2	0.418	-3.378	1.076
8	68.2	5.16	0.984	58.8	0.0947	57.2	0.983	-3.007	1.736
9	102.	5.18	1.58	58.0	0.0542	57.2	1.58	-2.801	1.980

NOTES: (1) Basic data are in Table LV.

(2) $K' = 9.7$.

TABLE XCIV

Zinc 4-picoline thiocyanate (0.005 M); picolinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	log [P]	log D
1	0	0	0	-	5.10	49.6	-	-
2	5.76	1.49	0.043	64.6	3.66	49.6	-4.367	-0.390
3	10.5	3.06	0.107	40.9	2.13	49.6	-3.971	0.158
4	17.2	4.15	0.172	51.7	1.05	49.6	-3.764	0.597
5	22.9	4.70	0.293	46.1	0.538	49.6	-3.533	0.942
6	28.6	4.94	0.378	49.5	0.299	49.6	-3.423	1.217
7	34.2	5.07	0.476	50.5	0.190	49.6	-3.322	1.427
8	68.0	5.19	1.14	50.5	0.0451	49.6	-2.943	2.061
9	101.	5.18	1.82	49.8	0.0271	49.6	-2.740	2.281

NOTES: (1) Basic data are in Table LVI.

(2) K' = 0.

TABLE XCV

Cadmium pyridine thiocyanate (0.001 M); extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	$[P] \times 10^3$	log [P]	log D
1	0	0	0	-	1.25	14.1	0	-	-
2	26.4	0.0306	1.92	13.7	1.22	14.3	1.85	-2.733	-1.600
3	38.9	0.122	2.83	13.6	1.12	14.4	2.73	-2.564	-0.963
4	52.8	0.318	3.63	14.2	0.957	14.5	3.53	-2.452	-0.479
5	65.8	0.536	4.39	14.5	0.728	14.6	4.30	-2.367	-0.133
6R	79.3	0.761	5.26	14.5	0.524	14.7	5.18	-2.286	0.161
7	92.1	0.909	6.04	14.6	0.348	14.7	5.98	-2.223	0.417
8	105.	1.04	6.99	14.4	0.238	14.7	6.95	-2.158	0.640
9	118.	1.10	7.68	14.8	0.154	14.7	7.65	-2.116	0.854
10	132.	1.17	8.61	14.8	0.129	14.7	8.58	-2.067	0.958
11	183.	1.24	11.9	14.9	0.027	14.7	11.9	-1.924	1.662

NOTES: (1) Basic data are in Table XLVI.
(2) Extraction 6R is the mean of 4 replicates.
(3) K' = 35.5.

TABLE XCVI

Cadmium pyridine thiocyanate (0.001 M); pyridinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	log [P]	log D
1	0	0	0	-	1.25	14.1	-	-
2	26.2	0.0243	1.76	14.8	1.24	14.4	-2.754	-1.708
3	39.4	0.119	2.63	14.8	1.13	14.5	-2.580	-0.979
4	52.5	0.311	3.50	14.6	0.950	14.7	-2.456	-0.485
5	65.4	0.540	4.30	14.7	0.728	14.8	-2.367	-0.130
6	78.5	0.757	5.12	14.7	0.525	14.9	-2.291	0.158
7	91.6	0.920	5.92	14.8	0.366	14.9	-2.228	0.400
8	105.	1.04	6.75	14.9	0.239	14.9	-2.171	0.638
9	117.	1.11	7.65	14.7	0.145	14.9	-2.116	0.884
10	130.	1.16	8.44	14.8	0.0992	14.9	-2.074	1.068
11	182.	1.26	11.7	15.1	0.0226	14.9	-1.932	1.747
12	233.	1.27	15.3	14.9	0.0112	14.9	-1.815	2.053

NOTES: (1) Basic data are in Table XLVII.

(2) $K' = 0$.

TABLE XCVII

Cadmium 3-picoline thiocyanate (0.001 M); picolinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	log [P]	log D
1	0	0	0	-	1.25	57.2	-	-
2	18.2	0.00910	0.288	63.1	1.24	57.2	-3.541	-2.135
3	34.1	0.130	0.594	56.5	1.13	57.2	-3.226	-0.940
4	45.5	0.382	0.760	57.9	0.882	57.2	-3.119	-0.364
5	56.7	0.628	0.966	56.1	0.647	57.2	-3.015	-0.013
6	68.0	0.861	1.15	56.1	0.423	57.2	-2.939	0.310
7	86.1	1.07	1.40	58.4	0.223	57.2	-2.854	0.681
8	102.	1.23	1.76	55.2	0.0652	57.2	-2.754	1.276
9	137.	1.26	2.23	59.2	0.0277	57.2	-2.652	1.658
10	204.	1.27	3.55	56.0	0.00895	57.2	-2.450	2.153

NOTES: (1) Basic data are in Table LVII.

(2) $K' = 0$.

TABLE XCVIII

Cadmium 4-picoline thiocyanate (0.001 M); picolinium chloride added; extraction into chloroform

Ext. No.	$[P]_{T,o} \times 10^3$	$[M]_{T,o} \times 10^3$	$[P]_{T,A} \times 10^3$	p*	$[M]_{T,A} \times 10^3$	p_t	log [P]	log D
1	0	0	0	-	1.25	49.6	-	-
2	11.4	0.0091	0.215	52.8	1.24	49.6	-3.668	-2.134
3	22.7	0.132	0.444	49.9	1.09	49.6	-3.353	-0.917
4	34.1	0.507	0.648	49.5	0.763	49.6	-3.188	-0.178
5	45.4	0.860	0.821	51.1	0.424	49.6	-3.086	0.308
6	56.6	1.06	1.06	49.4	0.205	49.6	-2.975	0.713
7	68.0	1.16	1.25	50.7	0.111	49.6	-2.903	1.021
8	85.8	1.25	1.60	50.5	0.0340	49.6	-2.796	1.566
9	101.	1.26	1.97	48.7	0.0136	49.6	-2.706	1.967
10	156.	1.28	3.04	49.6	0.002	49.6	-2.517	2.806

NOTES: (1) Basic data are in Table LVIII.

(2) $K' = 0.$

2. The Least-Squares Value of p**, and the 95 Percent Confidence Limits of p**

To find the best value of p**, a least-squares method was devised. To take into account the loosely-bonded pyridine (or picoline) in the organic phase it was first necessary to define another form of partition coefficient. It was defined as follows:

$$p_t = \frac{[P]_o + [P]_1}{[P]} \qquad (39)$$

where $[P]_o$ and $[P]_1$ are the concentrations in the organic phase of free pyridine (or picoline) and loosely-bonded pyridine (or picoline), respectively. At a pyridine (or picoline) concentration of zero, p_t is equal to p (the partition coefficient of pyridine or picoline in the absence of metal), since complexes then were absent from the organic phase. When the total pyridine (or picoline) concentration of the aqueous phase, $[P]_{T,A}$ was such that most of the metal was present in the organic phase, p_t became essentially constant. Between these limits of total pyridine (or picoline) concentration, p_t was arbitrarily taken to vary linearly with $[P]_{T,A}$. The relationship between p_t and $[P]_{T,A}$ is shown, for each metal pyridine and picoline thiocyanate extraction system, in Figs. 25 to 46.

It is shown in Part VI-2, from equations developed there, that

$$[P] = [P]_{T,A} - \frac{[M]_{T,A}\,[P]\,K'}{1 + [P]\,K'} \qquad (37)$$

and

$$\frac{p_t - p^*}{p^*} = \frac{[M]_{T,A} K'}{1 + [P] K'} \qquad (40)$$

from which

$$\lim_{[P]_{T,A} \longrightarrow 0} \frac{p_t - p^*}{p^*} = \frac{p - p^{**}}{p^{**}} = [M]_{T,A} K' \qquad (41)$$

where equation (41) defines p**.

For each of Figs. 25 to 46, a set of three to five values of p** were obtained by drawing smooth curves through the data and extrapolating them to $[P]_{T,A} = 0$. These curves fanned out so that the two outer curves encompassed almost all the points within their boundaries. Thus, three to five values of p** were obtained for each Figure. From equation (41), corresponding values of K' were found. These values are in Table XCIX. Then for each value of K' for a given Figure, the value of $[P]$ was computed from equation (37) for every value of $[M]_{T,A}$ (the total concentration of metal in the aqueous phase of the specified solvent-extraction system). The values of $[M]_{T,A}$, K', $[P]$ and p_t for each point were then substituted into equation (40), from which a value of p* was computed for each value of $[P]$, for a given K'. The computed value of p* was designated p^*_{calc}. For each value of p^*_{calc} there was a measured value of p*. Thus it was possible, for each point in the Figure, to calculate $(p^* - p^*_{calc})^2$, for a given K'. By summing these squares of differences over all the points in the Figure, for a given K', a quantity was obtained which measured the dispersion of the experimental points about the smooth curve corresponding to a given value of K', and an extrapolated value of p**.

TABLE XCIX

Trial values and best values of p** and K' for the metal pyridine and picoline thiocyanate extraction systems

Extraction system	p**	K'	$\sum(p^* - p^*_{calc})^2$	Best values		
				p**	K'	$\sum(p^* - p^*_{calc})^2$
0.0025-M Co; Py , T	14.1 13.5 13.0 12.5	0 17.3 33. 50.	3.35 0.73 0.84 2.63	13.3	23.3	0.50
0.0025-M Co; Py , T[a]	14.1 13.8 13.5 13.2	0 8.4 17.3 26.	0.88 0.45 0.49 0.83	13.7	11.3	0.42
0.0005-M Co; Py , T	14.1 14.0 13.9 13.8	0 13.8 28. 42.	0.34 0.31 0.32 0.34	13.96	19.4	0.305
0.0005-M Co; Py , T[a]	14.1 14.0 13.9	0 13.8 28.	0.22 0.31 0.48	14.15	Neg- ative	0.20
0.0025-M Co; 3-Pic , T	52.0 49.0 46.0 43.0	20. 45. 73. 106.	129.2 81.0 104.9 168.9	48.2	52.4	76.

(continued)

TABLE XCIX (continued)

Extraction system	p**	K'	$\sum(p^* - p^*_{calc})^2$	Best values		
				p**	K'	$\sum(p^* - p^*_{calc})^2$
0.0025-M Co; 3-Pic , T[a]	53.0 50.0 47.0	31. 56. 85.	36.7 24.1 60.9	50.5	51.6	22.
0.0025-M Co; 4-Pic , T	45.0 42.0 39.0 36.0	19. 46. 82. 121.	63.4 41.3 81.7 185.8	42.0	48.1	41.3
0.0025-M Co; 4-Pic , T[a]	49.0 48.0 47.0 46.0	4.8 13. 22. 30.	29.5 23.5 25.3 28.4	48.0	13.0	23.
0.005-M Ni; Py , T	11.0 10.0 9.0 8.0	55. 80. 111. 149.	43.0 27.0 20.1 22.0	8.5	129.	19.
0.005-M Ni; Py , T[a]	13.0 12.0 11.0 10.0	16.5 34. 55. 80.	10.8 4.76 3.78 9.08	11.4	46.3	3.0
0.0025-M Ni; Py , T	12.7 12.0 11.3 10.6	45 71 101 134	11.2 5.2 1.85 1.34	10.9	115.	1.0
0.0005-M Ni; Py , T	13.5 13.0 12.5 12.0	87. 166. 250. 342.	3.26 1.78 0.99 1.01	12.3	286.	0.90

(continued)

TABLE XCIX (continued)

Extraction system	p**	K'	$\sum (p^* - p^*_{calc})^2$	Best values		
				p**	K'	$\sum (p^* - p^*_{calc})^2$
0.005-M Ni; 3-Pic , T[a]	50.0 44.0 38.0 32.0	28. 59. 99. 154.	299.7 115.3 131.8 397.0	43.0	64.6	100
0.005-M Ni; 4-Pic , T[a]	40.0 35.0 30.0 25.0	47. 82. 128. 192.	139.9 53.7 82.3 251.4	33.0	98.3	50.
0.005-M Zn; Py , T	14.1 13.5 13.0 12.5 12.0	0 8.7 16.5 25. 34.	4.07 3.02 3.21 5.28 8.54	13.3	11.8	2.8
0.005-M Zn; Py , T[a]	14.1 13.5 13.0 12.5	0 8.7 16.5 25.	1.73 0.71 1.46 3.31	13.6	7.2	0.65
0.005-M Zn; 3-Pic , T[a]	57.2 53.0 49.0 45.0	0 15.5 33. 53.	98.3 96.1 141.3 205.2	54.5	9.7	90.
0.005-M Zn; 4-Pic , T[a]	49.6 45.0 41.0 37.0	0 20. 41. 67.	321.6 401.5 503.3 657.5	51.0	< 0	310.

(continued)

TABLE XCIX (continued)

Extraction system	p**	K'	$\sum(p^* - p^*_{calc})^2$	Best values		
				p**	K'	$\sum(p^* - p^*_{calc})^2$
0.001-M Cd; Py , T	14.1 13.7 13.3 12.9	0 23. 48. 75.	1.42 0.34 0.41 1.12	13.5	35.5	0.25
0.001-M Cd; Py , T[a]	14.1 13.7 13.3	0 23. 48.	0.41 1.16 2.87	14.3	< 0	0.30
0.001-M Cd; 3-Pic , T[a]	57.2 54.0 51.0	0 47. 97.	49.1 106.0 183.1	58.0	< 0	45.
0.001-M Cd; 4-Pic , T[a]	49.6 46.0 43.0	0 63. 123.	15.5 74.4 169.7	50.5	< 0	25

NOTES: (1) T means thiocyanate. The concentration of metal quoted is the initial value for the aqueous phase before equilibration.
(2) Py = pyridine; Pic = picoline.
(3) For the definition of K' see equation (36); for its calculation, see equation (41).
(4) p* is the apparent partition coefficient of pyridine or picoline in the metal pyridine (or picoline) thiocyanate extraction systems.
(5) p^*_{calc} is a computed value of p*.
(6) p** is the value of p* at zero pyridine (or picoline) concentration; K' and p** are related by equation (41).
(7) The best values of p** and $\sum(p^* - p^*_{calc})^2$ were obtained from a plot of $\sum(p^* - p^*_{calc})^2$ versus p**.

(continued)

TABLE XCIX (continued)

(8) The best value of K' was obtained by using the best value of p** in equation (41).
(9) The superscript "a" denotes extractions made in the presence of added pyridinium or picolinium chloride.

In this way, three to five values of $\sum(p^* - p^*_{calc})^2$ were obtained for the three to five chosen values of K'; they are given in Table XCIX. By plotting the value of p** corresponding to the minimum value of $\sum(p^* - p^*_{calc})^2$ was found. This was taken to be the "least-squares" value, that is, the best value. It is also given in Table XCIX.

An example of the calculations that were carried out to obtain the best value of p**, and hence of K' is given in Table C.

From the minimum value of $\sum(p^* - p^*_{calc})^2$ it was possible to obtain an estimate* of the 95 percent confidence limits of p**. Thus, the standard error of p**, $s_{p^{**}}$, was calculated from the equation

$$s_{p^{**}} = \sqrt{\frac{(p^* - p^*_{calc})^2}{N(N-1)}}$$

where N is the number of points in the specific Figure for which p** is required. By using these estimates for the standard error of p**, the 95 percent confidence limits of p** were calculated. These 95 percent confidence limits, and the best values for p** are given together in Table LX.

3. The Least-Squares Value of K', and the 95 Percent Confidence Limits of K'

The best value of K' was obtained by substituting the best value of p**, together with the known value for p and the known

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* The estimate strictly applies to the average difference between p* and p^*_{calc}. This is likely to be an optimistic estimate of the 95 confidence limits of the extrapolated value of p*, which is p**.

TABLE C

Detailed summary of calculation of $\sum (p^* - p^*_{calc})^2$ at different values of p** and K'. Example: 0.0025-M Co; Py , T

Ext. No.	$[P]_{T,A} \times 10^3$	$[M]_{T,A} \times 10^3$	p*	p** = 14.1 ; K' = 0			p** = 13.5 ; K' = 17.3		
				$[P] \times 10^3$	p^*_{calc}	$(p^*-p^*_{calc})^2$	$[P] \times 10^3$	p^*_{calc}	$(p^*-p^*_{calc})^2$
1	0	2.58	-	0	-	-	0	-	-
2	1.02	2.55	12.8	1.02	14.1	1.69	0.978	13.5	0.49
3	1.84	2.38	13.8	1.84	14.2	0.16	1.77	13.6	0.04
4R	2.68	1.89	13.7	2.68	14.2	0.25 x 4	2.60	13.8	0.01 x 4
5	3.48	1.28	13.6	3.48	14.2	0.36	3.41	13.9	0.09
6	4.17	0.799	14.0	4.17	14.3	0.09	4.12	14.1	0.01
7	4.94	0.461	14.2	4.94	14.3	0.01	4.90	14.2	0.00
8	5.76	0.272	14.3	5.76	14.3	0.00	5.74	14.2	0.01
9	6.64	0.169	14.3	6.64	14.3	0.00	6.62	14.3	0.00
10	10.3	0.0370	14.1	10.3	14.3	0.04	10.3	14.3	0.04
$\sum$						3.35			0.73

(continued)

TABLE C (continued)

Ext. No.	p** = 13.0 ; K' = 33.			p** = 12.5 ; K' = 50.		
	$[P]\times10^3$	p^*_{calc}	$(p^*-p^*_{calc})^2$	$[P]\times10^3$	p^*_{calc}	$(p^*-p^*_{calc})^2$
1	0	-	-	0	-	-
2	0.943	13.0	0.04	0.909	12.6	0.04
3	1.71	13.2	0.36	1.66	12.8	1.00
4R	2.53	13.4	0.09 x 4	2.47	13.1	0.36 x 4
5	3.35	13.7	0.01	3.30	13.5	0.01
6	4.08	14.0	0.00	4.04	13.8	0.04
7	4.88	14.1	0.01	4.85	14.0	0.04
8	5.72	14.2	0.01	5.70	14.2	0.01
9	6.61	14.2	0.01	6.60	14.2	0.01
10	10.3	14.3	0.04	10.3	14.3	0.04
$\sum$			0.84			2.63

NOTES: (1) The trial values of p** and K' are shown in the first row; these trial values and the best values are the first entered in Table XCIX.

(2) Where replicate extractions were carried out, each replicate was assigned a weight of unity; extraction 4R is the mean of 4 replicates.

(3) For definitions and equation references, see Notes in Table XCIX.

value of $[M]_{T,A}$ into equation (41). The best value is given in Table XCIX.

The 95 percent confidence limits of K' were found by using the upper and lower 95 percent confidence limits of p** in equation (41). These 95 percent confidence limits and the best values of K' are given together in Table LX.

Appendix XVII

The Calculation of Stepwise Formation Constants in the Organic Phase

1. Introduction

In Part VI-3 a method was described for the direct calculation of the stepwise formation constants of the metal tetrapyridine and tetrapicoline thiocyanates in the organic phase of the metal pyridine and picoline thiocyanate extraction systems. However, the calculations presented in this Appendix were carried out before the "least-squares" value of K' had been computed; therefore the values of $[P]$ and $[P]_o$, the concentrations of free pyridine (or picoline) in the aqueous and organic phases respectively, were very slightly in error*. In addition, the calculations presented in this Appendix were made prior to the discovery of loosely-bonded pyridine (or picoline) in the organic phase. However, the errors introduced by using slightly erroneous values of $[P]$ and $[P]_o$ should not seriously affect the calculations, and the qualitative conclusions that are drawn from the calculations.

2. Basis of Calculations, and Results

The detailed basis for the calculation of the stepwise formation constant, k_4, is given in Part VI-3. However, for convenience, this basis is briefly reviewed:

It is evident from the equation

$$z = \frac{\bar{n} - 2}{4 - \bar{n}} = k_4 [P]_o^2 \qquad (45)$$

* Only in this Appendix were slightly-erroneous balues of $[P]$ and $[P]_o$ used. Elsewhere the correct values are listed and were always used.

(where $\bar{n}$, the average number of pyridine or picoline ligands bound to each metal atom in the organic phase, is defined by equation (42)), that a plot of z versus $[P]_o^2$ gives a straight line with slope k_4.

For each extraction system the method of least-squares (101) was used to obtain the equation for the line of best fit*; z was plotted against $[P]_o^2$ when the dipyridinate (or dipicolinate) was the predominant species, and z^{-1} was plotted against $[P]_o^{-2}$ when the tetrapyridinate (or tetrapicolinate) was predominant. The value of z or its reciprocal was the dependent variable, and $[P]_o^2$ or its reciprocal was the independent variable. Each of the values of z (or z^{-1}) used was assigned a weight of unity; where replicate values of z (or z^{-1}) were available, a weight equal to the number of replicates was assigned.

The equations of the least-squares lines are given in Table CI. These equations, together with the standard deviations of the coefficients, allowed the 95 percent confidence limits of k_4 to be computed. From the values of k_4 and their 95 percent confidence limits, qualitative conclusions were drawn. The statistical arguments, together with the qualitative conclusions are given below.

3. Statistical Argument, and Qualitative Conclusions

From the data in Table CI it is seen that statistically-significant values of k_4 were obtained only for the following extraction systems: (1) zinc pyridine thiocyanate; (2) cadmium pyridine thiocyanate; and (3) cadmium pyridine thiocyanate in the presence of pyridinium chloride.

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* A digital computer (English Electric, Model KDF9) was used to obtain the equation for the line of best fit.

TABLE CI

Equations of least-squares lines, and k_4 values with their 95 percent confidence limits for metal pyridine and picoline thiocyanate extraction systems

Extraction system	Equation of least-squares lines	Standard error of coefficient	k_4	95 percent confidence limits of k_4	
				Upper	Lower
0.0025-M Co; Py , T	$z^{-1} = -0.847 \times 10^{-4} [P]_o^{-2}$	1.24×10^{-4}	-1.18×10^{4}	Infinity	0.498×10^{4}
0.0025-M Co; Py , T[a]	$z^{-1} = -0.629 \times 10^{-4} [P]_o^{-2}$	1.74×10^{-4}	1.59×10^{4}	Infinity	0.236×10^{4}
0.0025-M Co; 3-Pic , T	$z^{-1} = -3.14 \times 10^{-4} [P]_o^{-2}$	8.56×10^{-4}	$-0,319 \times 10^{4}$	Infinity	0.625×10^{3}
0.0025-M Co; 3-Pic , T[a]	$z^{-1} = 2.93 \times 10^{-4} [P]_o^{-2}$	9.45×10^{-4}	-0.341×10^{4}	Infinity	0.429×10^{3}
0.0025-M Co; 4-Pic , T	$z^{-1} = -0.727 \times 10^{-4} [P]_o^{-2}$	2.29×10^{-4}	-1.37×10^{4}	Infinity	0.225×10^{4}
0.0025-M Co; 4-Pic , T[a]	$z^{-1} = -0.261 \times 10^{-4} [P]_o^{-2}$	0.214×10^{-4}	-3.83×10^{4}	Infinity	3.00×10^{4}
0.005-M Ni; Py , T	$z^{-1} = -0.657 \times 10^{-5} [P]_o^{-2}$	0.317×10^{-5}	-1.52×10^{5}	Infinity	3.70×10^{4}
0.005-M Ni; Py , T[a]	$z^{-1} = -1.26 \times 10^{-5} [P]_o^{-2}$	0.461×10^{-5}	-0.793×10^{5}	Infinity	5.00×10^{4}
0.0025-M Ni; Py , T[b]	$z^{-1} = -0.540 \times 10^{-5} [P]_o^{-2}$	0.195×10^{-5}	-1.85×10^{5}	Infinity	5.00×10^{4}
0.0025-M Ni; Py , T[a,b]	$z^{-1} = 0.330 \times 10^{-5} [P]_o^{-2}$	0.190×10^{-5}	3.03×10^{5}	Infinity	0.872×10^{5}
0.005-M Ni; 3-Pic , T[a]	$z^{-1} = -2.43 \times 10^{-6} [P]_o^{-2}$	6.36×10^{-6}	-0.412×10^{6}	Infinity	0.763×10^{5}
0.005-M Ni; 4-Pic , T[a]	$z^{-1} = -0.893 \times 10^{-6} [P]_o^{-2}$	1.53×10^{-6}	-1.12×10^{6}	Infinity	0.328×10^{6}
0.005-M Zn; Py , T	$z = 38.0 [P]_o^{2}$	7.40	38.0	54.0	22.0

(continued)

TABLE CI (continued)

Extraction system	Equation of least-squares lines	Standard error or coefficient	k_4	95 percent confidence limits of k_4	
				Upper	Lower
0.005-M Zn; Py, T^a	$z = -149. [P]_o^2$	69.8	-149.	9.0	< 0
0.005-M Zn; 3-Pic , T^a	$z = 21.7 [P]_o^2$	30.9	21.7	97.3	< 0
0.005-M Zn; 4-Pic , T^a	$z = 8.78 [P]_o^2$	14.7	8.78	44.8	< 0
0.001-M Cd; Py , T	$z^{-1} = -3.02 \times 10^{-3} [P]_o^{-2}$	0.586×10^{-3}	-0.331×10^{3}	< 0	< 0
0.001-M Cd; Py , T^a	$z^{-1} = -9.12 \times 10^{-4} [P]_o^{-2}$	3.28×10^{-4}	-0.110×10^{4}	< 0	< 0
0.001-M Cd; 3-Pic , T^a	$z^{-1} = -2.99 \times 10^{-4} [P]_o^{-2}$	7.33×10^{-4}	-0.335×10^{4}	Infinity	0.699×10^{3}
0.001-M Cd; 4-Pic , T^a	$z^{-1} = 1.13 \times 10^{-4} [P]_o^{-2}$	0.93×10^{-4}	-0.885×10^{4}	Infinity	0.934×10^{4}

NOTES: (1) T means thiocyanate. The concentration of metal quoted is the initial value for the aqueous phase before equilibration.
(2) Py = pyridine; Pic = picoline.
(3) The superscript "a" denotes extractions made in the presence of added pyridinium or picolinium chloride.
(4) The superscript "b" denotes extractions made into benzene.
(5) For the definition of k_4, see equation (44).
(6) For the definition of z, see equation (45).
(7) Only the positive range of values for k_4 within the 95 percent confidence interval is stated explicitly.

The values of k_4 obtained for the two cadmium pyridine thiocyanate extraction systems were apt to be less reliable because these systems contained (1) the highest concentration of pyridine; and (2) the lowest concentration of metal in comparison to the other systems for which k_4 values are reported. This combination of circumstances leads to less reliable values of $\bar{n}$ (see equation (42)), z (a function of $\bar{n}$), and hence of k_4.

The value of k_4 for the zinc pyridine thiocyanate system is significantly different from zero*. However, neglecting the two cadmium pyridine thiocyanate systems discussed above, only one observation in 18 is statistically-significant; when selecting 95 percent confidence limits as statistical criteria, it is expected that one observation in 20 will be statistically-significant. The deviation in the computed value of k_4 from the reported value therefore may be attributed to chance.

Nevertheless, the true value of k_4 for the zinc pyridine thiocyanate system will undoubtedly be small. This statement is substantiated by the fact that the 95 percent confidence limits of k_4 include the value of zero for the following extraction systems: (1) zinc 3-picoline thiocyanate (2) zinc 4-picoline thiocyanate; and (3) zinc pyridine thiocyanate in the presence of added pyridinium chloride.

The values of k_4 found for the other** extraction systems lead to a different conclusion; although the 95 percent confidence limits of

* In Part VII-2 a value for k_4 of about 10 is reported from the literature. This value agrees fairly well with the value at the lower 95 percent confidence limit ($k_4 = 22$).

** (1) cobalt pyridine, 3-picoline and 4-picoline thiocyanates; (2) nickel pyridine, 3-picoline and 4-picoline thiocyanates (using either chloroform or benzene as solvent in the nickel pyridine thiocyanate system); and (3) cadmium 3-picoline and 4-picoline thiocyanates.

k_4 are reported in Table CI, these values include ± infinity*.

Nevertheless, the true values of k_4 for these systems will undoubtedly be large.

The following qualitative conclusions were therefore drawn: (1) zinc pyridine (or picoline) thiocyanate was extracted into chloroform almost exclusively as the dipyridinate (or dipicolinate); (2) the pyridine, 3-picoline and 4-picoline thiocyanates of cobalt, nickel and cadmium were extracted into chloroform almost exclusively as the tetrapyridinates (or tetrapicolinates); and (3) nickel pyridine thiocyanate was extracted into benzene almost exclusively as the tetrapyridinate.

These conclusions were confirmed by the calculation of k_4 from literature data; these values are reported in Part VII-2.

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* Since the coefficient in the least squares line is, in fact, k_4^{-1} for these systems, then since the 95 percent confidence limits of this coefficient include the value zero, k_4 may have a value of ± infinity. However, only the positive range of values for k_4 within the confidence interval is stated explicitly.

Appendix XVIII

The Overall Formation Constants of Metal-Pyridine, Metal-Picoline and Metal-Thiocyanate Complexes in Aqueous Solution

Introduction

As working data for the considerations in the present Appendix, the overall formation constants in aqueous solution were required for some metal pyridine (or picoline) and metal thiocyanate complexes. The constants for metal pyridine and metal picoline complexes are given in Table CII, those for metal thiocyanate complexes are given in Table CIII.

A. The Relative Proportions of Metal Pyridine (or Picoline) Complexes in the Aqueous Phases of the Metal Pyridine and Picoline Thiocyanate Extractions Systems

The ratios of the molar concentration of metal complex ion to molar concentration of free metal ion were calculated for the monopyridine (or monopicoline) and multipyridine (or multipicoline) complex ions of the metals cobalt, nickel, zinc and cadmium, in aqueous solution containing only the metal ion and pyridine (or picoline). The following equation was used:

$$\frac{[MP_m]}{[M]} = K_{m,o}[P]^m$$

where $[MP_m]$ is the concentration of the m^{th} metal pyridine (or picoline) complex, and $K_{m,o}$ is its overall formation constant in aqueous solution. The concentration of free pyridine (or picoline)

TABLE CII

The overall formation constants in aqueous solution for some divalent metal pyridine and metal picoline complex ions

Metal	Ligand	$K_{1,0}$	$K_{2,0}$	$K_{3,0}$	$K_{4,0}$	Reference
	Pyridine	13.8	73.2	-	-	(112)
Cobalt	3-Picoline	-	-	-	-	-
	4-Picoline	-	-	-	-	-
	Pyridine	60.3	677.	1380.	-	(112)
Nickel	3-Picoline	-	-	-	-	-
	4-Picoline	-	-	-	-	-
	Pyridine	12.3	49.0	85.2	-	(114)
Zinc	3-Picoline	17.0	79.5	151.	-	(114)
	4-Picoline	20.0	135.	708.	-	(114)
	Pyridine	17.8	85.2	191.	-	(114)
Cadmium	3-Picoline	25.1	144.	316.	-	(114)
	4-Picoline	31.6	141.	933.	-	(114)

NOTES: (1) $K_{m,n}$ is the equilibrium constant for the reaction

$$M + mP + nT = MP_mT_n.$$

(2) $K_{o,o}$ is unity.

TABLE CIII

The overall formation constants in aqueous solution for some divalent metal thiocyanate complexes

Metal	$K_{0,1}$	$K_{0,2}$	$K_{0,3}$	$K_{0,4}$
Manganese	5.37	70.8	-	-
Iron	8.92	1.17	-	-
Cobalt	8.92	39.8	63.2	0.50
Nickel	15.1	43.7	64.7	-
Copper	55.0	347.	490.	978.
Zinc	3.02	7.08	1.00	20.0
Cadmium	11.0	56.3	6.03	60.3

NOTES: (1) $K_{m,n}$ is the equilibrium constant for the reaction

$$M + mP + nT = MP_mT_n.$$

(2) $K_{0,0}$ is unity.

(3) Data are from reference (112).

was taken to be 1.0×10^{-3}M*.

The results of these calculations, given in Table CIV show that the monopyridinate (or monopicolinate) was the major complex species present at this concentration of free pyridine (or picoline); it is evident that, at lower concentrations of free pyridine (or picoline), even a higher proportion of the monopyridinate (or monopicolinate) would be present. Moreover, it is also seen from Table CIV that 6 percent or less of the total metal concentration was complexed by pyridine (or picoline) for any of the metals.

The ratios of the total molar concentration of metal thiocyanate complexes to molar concentration of free metal ion were calculated for several divalent transition metals, for an aqueous solution containing only the metal ion and thiocyanate ion. The following equation was used:

$$\sum_{n=1} \frac{[MT_n]}{[M]} = \sum_{n=1} K_{o,n} [T]^n$$

where $K_{o,n}$ is the overall formation constant in aqueous solution of the n^{th} metal thiocyanate complex. The concentration of free thiocyanate, $[T]$, was taken to be 0.27M (the total concentration of thiocyanate in the aqueous phase of extraction systems studied in the present investigation).

The results of these calculations, given in Table CV showed that, for the metals cobalt, nickel, zinc and cadmium (the metals studied in the present investigation) more than 85 percent of the metal was present as a metal thiocyanate complex**.

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* This concentration of free pyridine (or picoline) was chosen because in Figs. 25 to 46 it is seen that the apparent partition coefficient, p*, differed quite markedly from the partition coefficient, p, of the free ligand at total aqueous concentrations of pyridine (or picoline), $[P]_{T,A}$ of the order 10^{-3}M or less.

** For zinc, about 60 percent of the metal was complexed.

TABLE CIV

The molar ratio of complex ion to free metal ion and of the complex ion to the mono-substituted complex ion, for the metal pyridine (or picoline) complexes in aqueous solution

Metal (II)	Ligand	$\frac{[MP]}{[M]}$	$\frac{[MP_2]}{[M]}$	$\frac{[MP_3]}{[M]}$	$\frac{[MP_4]}{[M]}$	$\frac{[MP]}{[MP]}$	$\frac{[MP_2]}{[MP]}$	$\frac{[MP_3]}{[MP]}$	$\frac{[MP_4]}{[MP]}$	Fraction of total metal complexed
Cobalt	Pyridine	1.38×10^{-2}	7.32×10^{-5}	-	-	1.00	5.30×10^{-3}	-	-	0.014
Nickel	Pyridine	6.03×10^{-2}	6.77×10^{-4}	1.38×10^{-6}	-	1.00	1.12×10^{-2}	2.29×10^{-5}	-	0.060
	Pyridine	1.23×10^{-2}	4.90×10^{-5}	8.52×10^{-8}	-	1.00	3.98×10^{-3}	6.93×10^{-6}	-	0.012
Zinc	3-Picoline	1.70×10^{-2}	7.95×10^{-5}	1.51×10^{-7}	-	1.00	4.67×10^{-3}	8.88×10^{-6}	-	0.017
	4-Picoline	2.00×10^{-2}	1.35×10^{-4}	7.08×10^{-7}	-	1.00	6.75×10^{-3}	3.54×10^{-5}	-	0.026
	Pyridine	1.78×10^{-2}	8.52×10^{-5}	1.91×10^{-7}	-	1.00	4.78×10^{-3}	1.07×10^{-5}	-	0.018
Cadmium	3-Picoline	2.51×10^{-2}	1.44×10^{-4}	3.16×10^{-7}	-	1.00	5.64×10^{-3}	1.26×10^{-5}	-	0.025
	4-Picoline	3.16×10^{-2}	1.41×10^{-4}	9.33×10^{-7}	-	1.00	4.47×10^{-3}	2.95×10^{-5}	-	0.032

NOTES: (1) $K_{o,o}$ is unity.

(2) The ratios were calculated from the overall formation constants (Table CII) and a value of $[P] = 1.00 \times 10^{-3}$M

TABLE CV

The molar ratio of total complex ion to free metal ion for the metal thiocyanate complexes in aqueous solution

Metal (II)	$\sum_{n=1} \frac{[MT_n]}{[M]}$	Fraction of total metal complexed	Fraction of total metal uncomplexed
Manganese	6.62	0.87	0.13
Iron	2.50	0.71	0.29
Cobalt	6.55	0.87	0.13
Nickel	8.54	0.90	0.10
Copper	55.0	0.98	0.02
Zinc	1.47	0.60	0.40
Cadmium	7.53	0.88	0.12

NOTES: (1) $K_{o,o}$ is unity.

(2) The ratios were calculated from the overall formation constants (Table CIII) and a value of $[T] = 0.27M$.

The total metal concentration of the aqueous phase, $[M]_{T,A}$, was less than 5×10^{-3}M in every extraction experiment. For 80 percent of this metal complexed, the free metal concentration of the aqueous phase, $[M]$, was then less than 10^{-3}M.

From Table CIV, it is seen that the concentration ratio of metal monopyridine (or monopicoline) complexes to free metal ion never exceeded about 0.06 for a pyridine (or picoline) concentration of 10^{-3}M. Therefore, when $[M] = 10^{-3}$M, $[MP] = 6 \times 10^{-5}$M, and the concentration of pyridine (or picoline) bound as a monopyridine (or monopicoline) complex comprised less than 6 percent of the total pyridine (or picoline) concentration of the aqueous phase.

To consider this proportion of the total concentration of pyridine (or picoline) in the aqueous phase as being bound pyridine (or picoline) would not alone account for the observed differences between the extrapolated value, p**, of the apparent partition coefficient and the partition coefficient, p, of the free ligand. Therefore, the presence of a mixed metal pyridine (or picoline) thiocyanate complex was indicated.

B. <u>The Concentration of Free Thiocyanate in the Aqueous Phases of the Metal Pyridine and Picoline Thiocyanate Extraction Systems</u>

The total concentration of thiocyanate in the aqueous phase of every extraction system studied in the present investigation was about 0.27M. The concentration of free thiocyanate in the aqueous phase, $[T]$, was less than 0.27M for two reasons: (1) metal thiocyanate complexes formed in the aqueous phase; and (2) the metal was extracted into the organic phase of the extraction system as a metal pyridine (or picoline) thiocyanate complex.

It is the purpose of this Section of the Appendix to determine the combined effects of complexation and extraction on the concentration of total thiocyanate in the aqueous phase.

The total concentration of metal in the equilibrated aqueous phase of every extraction system was known for the case where pyridine (or picoline) was absent; here it was expected that the concentration of metal thiocyanate complexes* would be highest.

The concentration of each metal thiocyanate complex in the aqueous phase then was calculated by using the equation

$$[MT_n] = K_{o,n} [M] [T]^n$$

where $[MT_n]$ is the concentration of the n^{th} metal thiocyanate complex, and $K_{o,n}$ is its overall formation constant in aqueous solution. The concentration of free thiocyanate, $[T]$ was taken to be 0.27M. The free metal concentration in the aqueous phase, $[M]$ was found from the equation

$$[M] = [M]_{T,A} Q$$

where $[M]_{T,A}$ is the total concentration of metal in the aqueous phase and Q is the known fraction** of uncomplexed metal in an aqueous 0.27-M thiocyanate solution containing a metal ion.

The results of these calculations, given in Table CVI, showed that not more than 3.7 percent of the total thiocyanate concentration

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* Mixed metal pyridine (or picoline) thiocyanate complexes will not be considered; where these complexes predominate in the aqueous phase, the metal concentration of the aqueous phase is so small that a negligible amount of thiocyanate is complexed (see Appendix XVIIID).

** These fractions are given in Table CV, for each of the metals known to form extractable pyridine (or picoline) thiocyanates.

TABLE CVI

The molar concentration of metal thiocyanate complexes in an aqueous 0.3-M thiocyanate solution

Metal	$[M]_{T,A}$ $M \times 10^3$	Fraction of $[M]_{T,A}$ that is free metal ion	$[M]$	$[MT]$	$[MT_2]$	$[MT_3]$	$[MT_4]$	Percent of total thiocyanate complexed
Manganese	5.0	0.13	0.65	9.43×10^{-4}	3.36×10^{-3}	-	-	3.1
Iron	5.0	0.29	1.45	3.49×10^{-3}	1.30×10^{-4}	-	-	1.4
Cobalt	2.5	0.13	0.32	7.71×10^{-4}	9.28×10^{-4}	3.97×10^{-4}	8.51×10^{-7}	1.4
Nickel	5.0	0.10	0.50	2.04×10^{-3}	1.60×10^{-3}	6.40×10^{-4}	-	2.6
Copper	5.0	0.018	0.090	1.34×10^{-3}	2.28×10^{-3}	8.68×10^{-4}	4.68×10^{-4}	3.7
Zinc	5.0	0.40	2.00	1.64×10^{-3}	1.04×10^{-3}	4.00×10^{-5}	2.20×10^{-4}	1.7
Cadmium	1.0	0.12	0.12	3.56×10^{-4}	4.94×10^{-4}	1.44×10^{-5}	3.84×10^{-5}	0.56

NOTES: (1) $K_{o,o}$ is unity.

(2) Each concentration was calculated from the overall formation constant (Table CIII), the indicated value of $[M]$ and a value of $[T] = 0.27M$.

of the aqueous phase was bound as a metal thiocyanate complex.

When sufficient pyridine (or picoline) is present in a metal pyridine (or picoline) thiocyanate extraction system to extract essentially all the metal, then the concentration of metal thiocyanate complexes in the aqueous phase would be essentially zero. The concentration of total thiocyanate in the aqueous phase would then be reduced by 0.01M* (3.7 percent).

Since the concentration of metal thiocyanate complexes in the aqueous phase continuously decreases as the metal pyridine (or picoline) thiocyanate extracts, it is clear that the concentration of free thiocyanate in the aqueous phase is very nearly constant (to within $\pm$ 1.7%) for each aqueous phase of every metal pyridine (and picoline) thiocyanate extraction system.

In addition, experiments were carried out in which the concentration of total thiocyanate in the aqueous phase was varied by about 4 percent with no measurable effect on the distribution ratio of cobalt in both cobalt 3-picoline and 4-picoline thiocyanate extraction systems. These experiments are summarized in Part V-3-4.

Finally, in Appendix XVIIIC it is shown that a $\pm$ 2 percent variation in the free thiocyanate concentration would have at most a $\pm$ 1 percent effect on the distribution ratio of the metal.

Therefore the concentration of free thiocyanate in the aqueous phase of the metal pyridine and picoline thiocyanate extraction systems was taken to be the total thiocyanate concentration of that phase, with negligible error.

* The largest total concentration of metal in the aqueous phase was 5×10^{-3}M; two moles of thiocyanate are extracted with every mole of metal (see Part V-3-4).

C. The Effect of Variations in the Free Thiocyanate Concentration of the Aqueous Phase on the Distribution Ratios of the Metals

It has been shown in Part VI-4 that

$$D = \frac{p_2 K_{2,2} (1 + B[P]^2) [P]^2}{A + f[P]} \qquad (52)$$

where D is the distribution ratio of the metal, $[P]$ is the concentration of free pyridine (or picoline) in the aqueous phase,

$$B = \frac{p_4 K_{4,2}}{p_2 K_{2,2}} \qquad (51)$$

$$p_n = \frac{[MP_nT_2]_o}{[MP_nT_2]} \qquad (47,48)$$

$$K_{m,n} = \frac{[MP_mT_n]}{[M][P]^n[T]^n} \qquad (49)$$

$$A = \sum_{n=o} K_{o,n} [T]^{n-2} \qquad (53)$$

and

$$f[P] = \sum_{m=1} K_{m,o} [P]^m [T]^{-2} + \sum_{r=1} K_{r,1} [P]^r [T]^{-1} + \ldots . \qquad (54)$$

It is shown in Appendix XVIIID that

$$f\,[P] = [P]\,K'A \qquad (90)$$

so that

$$A + f\,[P] = A\,(1 + [P]\,K')$$

where K' is a constant defined by equation (36). Therefore, at a given value for $[P]$, the distribution ratio depends critically upon A.

It has been shown in Appendix XVIIIB that the concentration of free thiocyanate in the aqueous phase of the metal pyridine (or picoline) thiocyanate extraction systems may be taken as being essentially constant, and to have a value of 0.27M.

Now the values of A were calculated, for each of the metals which are known to form extractable metal pyridine and picoline thiocyanates, by using the values for the overall formation constants of metal thiocyanate complexes in aqueous solution, together with arbitrarily-chosen values for $[T]$ of 0.26M and 0.27M.

The results, given in Table CVII, show that the value of A changes by less* than $\pm$ 1 percent for a $\pm$ 2 percent change in $[T]$.

D. <u>The Effect of the Free Pyridine (or Picoline) Concentration in the Aqueous Phase on the Ratio R_2</u>

The ratio R_2 is defined as follows:

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* Except for zinc and iron, for which the value of A changes by about $\pm$ 2 percent for a $\pm$ 2 percent change in $[T]$.

TABLE CVII

Values of computed constants for metal thiocyanate complexes

Metal (II)	$\sum_{n=0} K_{o,n}[T]^{n-2} = A$		log A		$A[T]^2$	
	$[T] = 0.27M$	$[T] = 0.26M$	$[T] = 0.27M$	$[T] = 0.26M$	$[T] = 0.27M$	$[T] = 0.26M$
Manganese	104.	106.	2.02	2.03	7.62	7.18
Iron	47.9	50.3	1.68	1.70	3.50	3.40
Cobalt	103.	105.	2.01	2.02	7.55	7.11
Nickel	131.	133.	2.12	2.12	9.54	9.01
Copper	749.	753.	2.87	2.88	54.6	50.8
Zinc	33.8	35.2	1.53	1.55	2.47	2.38
Cadmium	117.	119.	2.07	2.08	8.53	8.05

NOTES: (1) $K_{m,n}$ is the equilibrium constant for the reaction

$M + mP + nT = MP_mT_n$.

(2) $K_{o,o}$ is unity.

(3) Values for $K_{o,n}$ are from Table CIII.

(4) $[T]$ is the free thiocyanate concentration in the aqueous phase.

$$R_2 = \frac{[P]\, f'[P]}{A + f[P]} \qquad (57)$$

where

$$A = \sum_{n=0} K_{o,n} [T]^{n-2} \qquad (53)$$

$$f[P] = [T]^{-2} \sum_{m=1} K_{m,o} [P]^m + [T]^{-1} \sum_{r=1} K_{r,1} [P]^r + \ldots. \qquad (54)$$

and

$$[P]\, f'[P] = [T]^{-2} \sum_{m=1} m\, K_{m,o} [P]^m + [T]^{-1} \sum_{r=1} r\, K_{r,1} [P]^r + \ldots. \qquad (87)$$

It has been shown in Appendix XVIIIA that the complex species MP would have been present in the aqueous phases of the extraction systems in much higher concentration than would the species MP_m ($m > 1$). Because of this fact it was suggested that the complex species MPT_n ($n > 0$) were likely to be present in the aqueous phase in much higher concentrations than were the species MP_rT_m ($r > 1$, $n > 0$). For the case where only monopyridine (or monopicoline) complexes (mixed or otherwise) are considered to be present in the aqueous phase

$$[T]^2 f[P] = [T]^2 [P]\, f'[P] = \frac{[MP]}{[M]} + \sum_{n=1} \frac{[MPT_n]}{[M]} \qquad (88)$$

For this case it may also be shown from equation (36) that

$$\frac{[MP]}{[M]} + \sum_{n=1} \frac{[MPT_n]}{[M]} = [P]\, K' \sum_{n=o} \frac{[MT_n]}{[M]} \qquad (89)$$

Combination of equations (53), (88) and (89) gives

$$f[P] = [P]\, f'[P] = [P]\, K'A \qquad (90)$$

and from equations (57) and (90)

$$R_2 = \frac{[P]K'}{1 + [P]\, K'} \qquad (58)$$

From equation (58) it is seen that the ratio R_2 depends only upon the free pyridine (or picoline) concentration in the aqueous phase of the metal pyridine (or picoline) thiocyanate extraction system. As $[P]$ approaches zero, R_2 approaches zero; as $[P]$ increases, R_2 approaches unity.

PART IX

LITERATURE CITED

1. G.H. Morrison and H. Freiser. Solvent extraction in analytical chemistry. John Wiley and Sons, Inc., New York. 1957.

2. Y. Marcus. Chem. Rev. 63, 139 (1963).

3. H.M. Irving and R.J.P. Williams. J. Chem. Soc. 1841 (1949).

4. H.M. Irving, F.J.C. Rossotti and R.J.P. Williams. J. Chem. Soc. 1906 (1955).

5. G. Spacu. Bull. Soc. Stunte Cluj. 1, 284 (1922).

6. G. Spacu and J. Dick. Z. Anal. Chem. 71, 97 (1927).

7. G. Spacu and J. Dick. Z. Anal. Chem. 71, 442 (1927).

8. P. Spacu. Z. Anal. Chem. 45, 423 (1939).

9. G. Spacu and J. Dick. Bull. Soc. Stunte Cluj. 4, 177 (1928).

10. G. Spacu and J. Dick. Bull. Soc. Stunte Cluj. 4, 241 (1928).

11. T. Moeller and R.E. Zogg. Anal. Chem. 22, 613 (1950).

12. M. Jean. Bull. Soc. Chim. France, 12, 437 (1945).

13. G.H. Ayres and S.S. Baird. Talanta, 7, 237 (1961).

14. J.H.W. Forsythe, R.J. Magee and C.L. Wilson. Talanta, 1, 249 (1958).

15. J.H.W. Forsythe, R.J. Magee and C.L. Wilson. Talanta, 3, 324 (1960).

16. J.A. Hunter and C.C. Miller. Analyst, 81, 79 (1956).

17. A. Weissburger. Technique of organic chemistry. Vol. VII, p. 411. Interscience Publishers, Inc., New York. 1955.

18. R.G. Pearson and D.C. Vogelsong. J. Am. Chem. Soc. 80, 1038 (1958).

19. C.N. Sideri and A. Osol. J. Am. Pharm. Assoc. Sci. Ed. 42, 586 (1953).

20. D.G. Leis and B.C. Curran. J. Am. Chem. Soc. 67, 79 (1945).

21. C.T. Kyte, G.H. Jeffery and A.I. Vogel. J. Chem. Soc. 4454 (1960).

22. H.C. Brown and X.R. Mihm. J. Am. Chem. Soc. 77, 1723 (1955).

23. W. Herz. Berichte, 31, 2671 (1898).

24. J. Stary. The solvent extraction of metal chelates. Pergamon Press. 1964.

25. H. Irving and C.F. Bell. J. Chem. Soc. 1216 (1952).

26. E. Knobloch. Collection Czech. Chem. Commun. 12, 407 (1947).

27. I.M. Kolthoff and V.A. Stenger. Volumetric analysis. Volume II, p. 57. Interscience Publishers, Inc., New York. 1947.

28. I.M. Kolthoff and E.B. Sandell. Textbook of quantitative inorganic analysis. The Macmillan Company, New York. 1952. p. 541.

29. G. Spacu and J. Dick. Bull. Soc. Stunte Cluj. 4, 431 (1929).

30. C.W. Pifer, E.G. Wollish and M. Schmall. Anal. Chem. 25, 310 (1953).

31. C.W. Pifer, E.G. Wollish and M. Schmall. Anal. Chem. 26, 215 (1954).

32. J.S. Fritz. Anal. Chem. 22, 578 (1950).

33. G.R. Makepeace and C.H. Craft. Ind. Eng. Chem. Anal. Ed. 16, 375 (1944).

34. A. Claassen and L. Bastings. Rec. Trav. Chim. 73, 783 (1954).

35. E.B. Sandell. Colorimetric determination of traces of metals. Interscience Publishers, Inc., New York. 1959. p. 669.

36. M.A. Rosanoff and A.E. Hill. J. Am. Chem. Soc. 29, 1467 (1907).

37. F.W. Bruckmiller. J. Am. Chem. Soc. 38, 1953 (1916).

38. W.F. Harris and T.R. Sweet. Anal. Chem. 24, 1062 (1952).

39. F.J. Welcher. The analytical uses of EDTA. D. Van Nostrand Co., Inc., New York. 1958. p. 230.

40. G. Schwarzenbach. Complexometric titrations. Interscience Publishers, Inc., New York. 1960. p. 78.

41. H. Flaschka. Mikrochim. Acta, 39, 38 (1952).

42. E.B. Sandell. Colorimetric determination of traces of metals. Interscience Publishers, Inc., New York. 1959. p. 413.

43. E.B. Sandell. Colorimetric determination of traces of metals. Interscience Publishers, Inc., New York. 1959. p. 419. Procedure A.

44. W. Biedermann and G. Schwarzenbach. Chimia, 2, 56 (1948); Chem. Abstr. 42, 3694 (1948).

45. F.J. Welcher. The analytical uses of EDTA. D. Van Nostrand Co., Inc., New York. 1958. p. 149.

46. N. Stafford. Analyst, 78, 733 (1953).

47. H.E. Williams. Cyanogen compounds. Edward Arnold and Co., London. 1948. p. 307.

48. R.A. Day, Jr. and A.L. Underwood. Quantitative analysis. Laboratory manual. Prentice-Hall, Inc., Englewood Cliffs, New Jersey. 1958. p. 62.

49. L. Meites and H.C. Thomas. Advanced analytical chemistry. McGraw-Hill Book Company, Inc., New York. 1958. p. 45.

50. E.H. Swift, M.G. Arcand, R. Lutwack and D.J. Meier. Anal. Chem. 22, 306 (1950).

51. W. Seaman and E. Allen. Anal. Chem. 23, 592 (1951).

52. H.T.S. Britton. Hydrogen ions. D. Van Nostrand Co., Inc., New York. 1929. p. 251.

53. I.M. Kolthoff. University of Minnesota. Private communication.

54. H.E. Williams. Cyanogen compounds. Edward Arnold and Co., London. 1948. p. 285.

55. G. Charlot. Qualitative inorganic analysis. Methuen and Company, Limited, London. 1953. p. 194.

56. H.A. Laitinen. Chemical analysis. McGraw-Hill Book Company, Inc., New York. 1960. p. 40.

57. J. Bjerrum, G. Schwarzenbach and L.G. Sillen. Stability constants: Part I, Organic ligands. p. 28; Part II, Inorganic ligands. p. 37. The Chemical Society, London. 1957.

58. J. Wong. Unpublished results from this laboratory.

59. J.H. Hildebrand. Solubility of non-electrolytes. American Chemical Society Monograph Series. Reinhold Publishing Corporation, New York. 1936. p. 138.

60. J.R. Partington. A textbook of inorganic chemistry. Macmillan and Co., Limited, London. 1953. p. 506.

61. S. Glasstone. The elements of physical chemistry. D. Van Nostrand Co., Inc., New York. 1957. p. 107.

62. I.M. Kolthoff and E.B. Sandell. Textbook of quantitative inorganic analysis. The Macmillan Company, New York. 1952. p. 37.

63. A.L. Edwards. Statistical methods for the behavioral sciences. Rinehart and Co., Inc., New York. 1956. p. 254.

64. A.L. Edwards. Statistical methods for the behavioral sciences. Rinehart and Co., Inc., New York. 1956. p. 278.

65. E.B. Mode. Elements of Statistics. Prentice-Hall, Inc., New York, 1953. p. 190.

66. H. Irving and R.J.P. Williams. J. Chem. Soc. 3192 (1953).

67. International critical tables. Vol. III, p. 427. McGraw-Hill Book Company, Inc., New York. 1928.

68. W. Banks. Trans. Fara. Soc. 33, 215 (1937).

69. E. Cartmell and G.W.A. Fowles. Valency and molecular structure. Butterworths Scientific Publications, London. 1956. p. 219.

70. L. Meites. Handbook of analytical chemistry. McGraw-Hill Book Company, Inc., New York. 1963. Section I, p. 47.

71. A. Hantzsch. Z. Anorg. Chem. 159, 273 (1927).

72. International conference on co-ordination chemistry, London, 1959. The Chemical Society, London. 1959. p. 153.

73. N.S. Gill and R.S. Nyholm. J. Inorg. Nucl. Chem. 18, 88 (1961).

74. I.M. Kolthoff and E.B. Sandell. Textbook of quantitative inorganic analysis. The Macmillan Company, New York. 1952. p. 456.

75. F.J.C. Rossotti and H. Rossotti. The determination of stability constants. McGraw-Hill Book Company, Inc., New York. 1961. Chapter 10.

76. I.M. Kolthoff and P.J. Elving. Treatise on analytical chemistry. Interscience Publishers, Inc., New York. 1961.

77. W.D. Treadwell and A. Ammann. Helv. Chim. Acta, 21, 1249 (1938).

78. R.E. Kirk and D.F. Othmer. Encyclopedia of chemical technology. Volume 4, p. 327. The Interscience Encyclopedia, Inc., New York. 1949.

79. W.T. Richards and J.H. Wallace. J. Am. Chem. Soc. 54, 2705 (1932).

80. International critical tables. Volume III, p. 387. McGraw-Hill Book Company, Inc., New York. 1928.

81. A. Seidell. Solubilities of inorganic and organic compounds. D. Van Nostrand Co., Inc., New York. 1919. p. 248.

82. W.F. Harris and T.R. Sweet. Anal. Chem. 26, 1649 (1954).

83. E.B. Sandell. Colorimetric determination of traces of metals. Interscience Publishers, Inc., New York. 1959. p. 451.

84. J. Ferguson. J. Chem. Phys. 32, 528 (1960).

85. G. Spacu and J. Dick. Z. Anal. Chem. 74, 188 (1928).

86. G. Spacu. Bull. Soc. Stunte Cluj. 1, 314 (1922).

87. G. Spacu. Bull. Soc. Stunte Cluj. 1, 352 (1922).

88. G. Spacu and J. Dick. Bull. Soc. Stunte Cluj. 4, 23 (1928).

89. G. Spacu and J. Dick. Z. Anal. Chem. 78, 241 (1929).

90. J. Golse. Bull. Soc. Pharm. Bordeaux, 71, 126 (1933).

91. G. Spacu and J. Dick. Z. Anal. Chem. 71, 185 (1927).

92. R.H. Muller and A.T. Burstell. Mikrochim. Acta, 28, 209 (1940).

93. G. Spacu and J. Dick. Z. Anal. Chem. 73, 356 (1928).

94. G. Spacu. Bull. Soc. Stunte Cluj. 1, 364 (1922).

95. H.C. Brown and A. Cahn. J. Am. Chem. Soc. 77, 1715 (1955).

96. R. Larsson and A. Miezis. Acta Chem. Scand. 19, 47 (1965).

97. S.M. Nelson and T.M. Shepherd. Inorg. Chem. 4, 813 (1965).

98. H.C.A. King, E. Koros and S.M. Nelson. J. Chem. Soc. 5449 (1963).

99. S.M. Nelson and T.M. Shepherd. J. Chem. Soc. 3276 (1965).

100. D.P. Graddon and E.C. Watton. Australian J. Chem. 18, 507 (1965).

101. A.L. Edwards. Statistical methods for the behavioral sciences. Rinehart and Co., Inc., New York. 1956. p. 122.

102. J.H.W. Forsythe, R.J. Magee and C.L. Wilson. Talanta, 3, 330 (1960).

103. E.B. Mode. Elements of statistics. Prentice-Hall, Inc., New York. 1953. p. 202.

104. F.J. Welcher. Organic analytical reagents. Volume 3, Chapter 1: D. Van Nostrand Co., Inc., New York. 1955.

105. C. Duval. Inorganic thermogravimetric analysis. Elsevier Publishing Co., London. 1963. pps. 227, 325, 447, 508, 519, 637, 660.

106. F.J. Welcher. Organic analytical reagents. Volume 3, p. 17. D. Van Nostrand Co., Inc., New York. 1955.

107. W.W. Windlandt and S.I. Ali. Z. Anorg. Chem. 337, 6 (1965).

108. L.M. Vallarino, W.E. Hill and J.V. Quagliano. Inorg. Chem. 4, 1598 (1965).

109. W. Libus and I. Uruska. Inorg. Chem. 5, 256 (1966).

110. J.R. Allan, D.H. Brown, R.H. Nuttall and D.W.A. Sharp. J. Inorg. Nucl. Chem. 26, 1895 (1964).

111. J.R. Allan, D.H. Brown, R.H. Nuttall and D.W.A. Sharp. J. Inorg. Nucl. Chem. 27, 1529 (1965).

112. L.G. Sillen and A.E. Martell. Stability constants of metal-ion complexes. Special publication no. 17 of the Chemical Society, London. 1964. p. 118-123; 440-441; 475-476.

113. S.M. Nelson and T.M. Shepherd. J. Chem. Soc. 3284 (1965).

114. A.G. Desai and M.B. Kabadi. Rec. Trav. Chim. 84, 1066 (1965).

115. A.G. Desai and M.B. Kabadi. J. Ind. Chem. Soc. 38, 10 (1961).

116. C. Golumbic and M. Orchin. J. Am. Chem. Soc. 72, 4145 (1950).

117. R. Collander. Acta Chem. Scand. 3, 717 (1949).

118. H.C.A. King, E. Koros and S.M. Nelson. J. Chem. Soc. 4832 (1964).

119. G. Simmons. Department of Chemistry, McGill University. Private communication.

120. L.H. Vogt, H.M. Faigenbaum and S.E. Wiberley. Chem. Rev. 269 (1963).

121. O.L. Harle and M. Calvin. J. Am. Chem. Soc. 68, 2612 (1946).

122. E. Cartmell and G.W.A. Fowles. Valency and molecular structure. Butterworths Scientific Publications, London. 1956. p. 196-207.

123. L. Pauling. The nature of the chemical bond. Cornell University Press. 1960. Chapters 7 and 8.

124. M.R. Rosenthal and R.S. Drago. Inorg. Chem. 4, 840 (1965).

125. A. Weissburger. Technique of organic chemistry. Vol. III, Part I, p. 332. Interscience Publishers, Inc., New York. 1956.