

KINETICS OF SOLVENT EXTRACTION

A thesis submitted for the degree of Doctor of Philosophy

by

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A B S T R A C T

A suitable experimental system was chosen for the study of the Kinetics of Solvent Extraction and the characteristics of the cell design were evaluated by studying the rate of transfer of 8-hydroxyquinoline from buffered solutions into paraffin. The rate was found to be first order with respect to 8-hydroxyquinoline, linearly related to stirring speed and interfacial area and to have an activation energy of 3.5 kcal per mol.

A survey was made of the rates involved in various organo-metallic extraction systems and the systems involving the stripping of copper, nickel and cobalt from di-2-ethylhexyl-phosphoric acid (D.E.H.P.) in paraffin were chosen for further study. These systems were chosen because they all had appreciably slower transfer rates than that of 8-hydroxyquinoline, whilst being amenable to closely controlled experimentation.

Using the relation between stirring rate and mass transfer rate, values of the bulk phase transfer resistance and the interfacial resistance, for the above systems, were found under varying experimental conditions and the relative significance of these two resistances was determined. It was found that the relative significance of the bulk phase resistance and interfacial resistance was dependent on the experimental conditions used in particular on the levels of pH and D.E.H.P. concentration.

The variation of bulk phase resistance with experimental conditions followed closely that predicted theoretically. The effect of the experimental conditions on the value of the interfacial resistance was not determined conclusively. However, sufficient evidence was accumulated to put forward a tentative suggestion for a rate determining step, based on the phenomena of steric hindrance.

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1.

I N T R O D U C T I O N1.1 GENERAL INTRODUCTION

1.1.0 Solvent extraction is a well established technique for laboratory chemical separation, and it has been applied to a wide variety of systems. In the petrol and nuclear fuel industries it is used as a production technique on a large scale.

With the advent of nuclear energy it became necessary to produce appreciable quantities of exceptionally pure metals and compounds of the lesser known metals; in particular uranium and thorium. Initially, in view of the price guarantees provided by the United States and British Atomic Energy Authorities, cost was not at a premium, quantity and quality being more important. This stimulated the search for techniques not previously used in extractive metallurgy. The highly successful techniques of solvent extraction and ion exchange of metal species, used by the analytical chemist, were scaled up along lines established in the chemical industry. The successful application of solvent extraction in uranium production led to the search for new and cheaper solvents which could be used for extracting other valuable metal species.

In metal extraction, the metal species is invariably extracted from an aqueous solution into an organic solvent. The reagent which forms the extractable compound may be in the aqueous phase, e.g. nitrate ions in the extraction of uranium into tri-butyl phosphate (TBP), or in the organic phase, e.g. naphthenic acid in paraffin for the extraction of copper.

The metal species is removed or "stripped" from the organic phase by a second aqueous solution, the latter then goes to further processing and the organic phase is recycled.

In scientific studies of the extraction of metal, species emphasis has been placed on equilibrium measurements and little attention has been given to the kinetics of extraction and stripping, although qualitative observations have indicated that some of the processes may be abnormally slow.

The objectives of the work described in this thesis were :-

- (i) To compare the rates of a number of metal extraction and stripping processes and to confirm that some were slow.
- (ii) To study a few selected slow processes in more detail in order to establish the factors which control their rates.
- (iii) If possible to suggest methods of improving the processes from a kinetic point of view.

The remaining parts of this general introduction will be used to describe briefly some of the metal extraction systems used or proposed, the phenomena encountered, and to introduce the essential stages in the extraction of a species from one solvent into another describing how they may influence the rate of the process.

1.1.1 Solvent Systems

The majority of extracting agents dissolved in the organic phase, which are used industrially for metal extraction, can be divided into four main groups :-

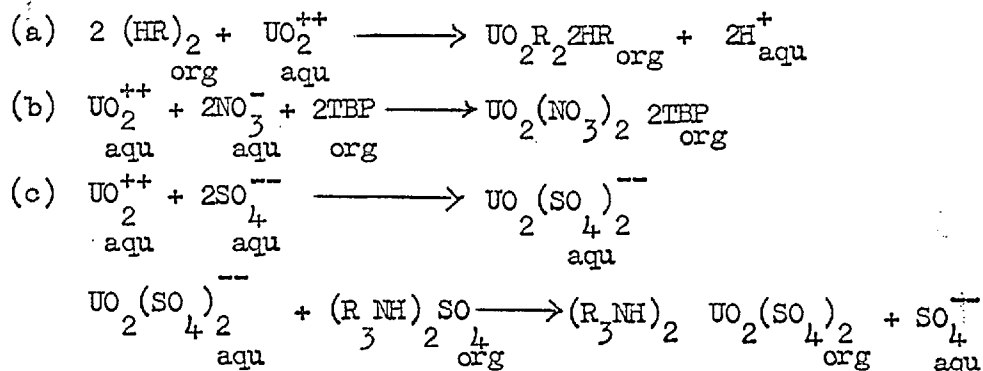
- (a) organo-carboxylic acids
- (b) organo-phosphoric acids
- (c) neutral organo-phosphorus compounds
- (d) secondary and tertiary amines

The reagents most commonly used, because of efficiency of separation and commercial availability, are naphthenic acid, di-2-ethylhexyl-phosphoric acid (D.E.H.P.), tri-butyl phosphate (T.B.P.) and tri-iso-octylamine (T.I.O.) respectively in each group. In all commercial processes paraffin is used as a diluent for these reagents. However, Fletcher^{1,2}, gives details of a method of purification of niobium and tantalum using undiluted T.B.P., a similar process has also been given for the purification of thorium nitrate³.

1.1.2 Nature of Extracting Compounds

D.E.H.P., T.B.P. and T.I.O. have found wide application in the purification of uranium and the equilibrium chemistry for all three systems has been thoroughly studied.⁴⁻¹⁷

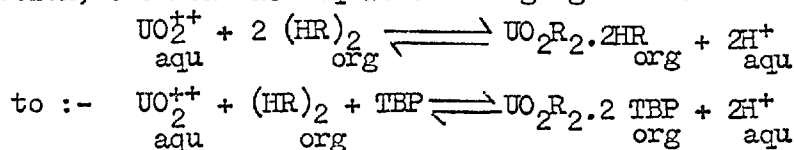
The principal equilibrium equations for the three systems are as follows :-



where $(\text{HR})_2$ is a dimerised molecule of D.E.H.P. and $(\text{R}_3\text{NH})_2 \text{SO}_4$ is tri-iso-octylamine in the sulphate form. There is adequate evidence for writing (D.E.H.P.) in the dimerised form.

The above equations only apply to low solvent loadings; the solvent loading being a measure of the number of molecules of the metal species extracted in relation to the total number of extractant molecules available.

In extractions at low solvent loadings, in addition to the valency bonding, the co-ordination shell of the metal is completed by undissociated solvent molecules, e.g. as in $\text{UO}_2 \text{R}_2 \cdot 2 \text{HR}$, where the two anions R complete the valency bonding and the two solvent molecules 2HR are the solvating molecules. However, at high solvent loadings this structure no longer applies and a polymerised species is formed of the type $(\text{UO}_2 \text{R}_2)_n \cdot 2 \text{HR}$. This phenomenon of polymerisation is not restricted to complexes with D.E.H.P. and uranium 18. In extractions with D.E.H.P. it has been found that addition of a small quantity of a neutral organic phosphate, e.g. T.B.P. can produce significantly greater extractions, this phenomenon being known as synergism. The mechanism of this effect is, as yet, uncertain. Kennedy 19 has put forward the theory that there is a change in the chemistry of the extraction, the reaction equation changing from :-



Since only one dimer of $(\text{HR})_2$ has to be dissociated, there is a saving of 8kcal per mol. This theory would appear to demand higher concentrations of T.B.P. than are normally found necessary and so is only partly correct. Also, there is evidence that the complexes involved in these extractions have the compositions $\text{UO}_2 \text{R}_2 \cdot \text{HR}$ and $\text{UO}_2 \text{R}_2 \cdot \text{TBP}$ in the absence and presence of T.B.P. respectively. So a further suggestion by Kennedy 20 that the excess molecules of (HR) or (T.B.P.) bring the metal atom up to its maximum co-ordination number of 8, is not upheld.

Another theory, of Irving and Edgington, claims that a synergist will be any compound which can co-ordinate with the original complex more strongly than water, thus giving the complex a higher organic phase solubility.

In some extractions the metal complex forms a third phase, e.g. the complex of the cobalti-chloride ion with tri-iso-octylamine. In such cases the complex can be made soluble in the organic phase by the addition of 5-10% by volume of a medium length organic alcohol, e.g. 2-ethylhexyl alcohol.

1.1.3 Kinetics

A chemical process may be divided into a number of stages which occur consecutively. When the rates of these stages are essentially the same, the system undergoes no rapid fluctuations and is said to be in a steady state. The rate of any of these stages taken alone may be slower than the others. This stage is known as the rate controlling stage. The process of solvent extraction can be divided into three stages. These stages are:-

- (1) Transfer of the reacting species from the bulk of any phase to the interface.
- (2) Transfer across the interface. This may be accompanied by a chemical reaction, or, at least, by a change in solvation of the transferred species.
- (3) Transfer of the products away from the interface.

The resistance to transfer due to stage 2 is known as the interfacial resistance. The interfacial resistance may be due to an activation energy or to a stereochemical effect, i.e. the orientation of the species at the interface. As with homogeneous chemical reactions, temperature may have a profound effect on the rate of any of the stages; the relationship between rate and temperature normally fits the exponential equation

$$k = A \exp (-E_a/RT)$$

1

where k is the reaction rate constant, E_a the activation energy, R the gas constant, T the absolute temperature and A is a constant. For stages 1 and 3, involving physical changes, E_a is small, less than 5 kcal mol⁻¹, whereas for a chemical reaction E_a may be much larger.

The absolute reaction rate theory of Glasstone, Eyring and Laidlaw²¹ may be applied to the stage of transfer across the interface. This theory proposes that the rate determining step

is the reversible formation of an activated complex which then breaks down into the reaction products. The relationship between reaction rate constant and temperature is given by the equation

$$k = (k'T/h) \exp(-\Delta G^\ddagger/RT) = (k'T/h) \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R) \quad 2.$$

where ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger are the entropy, heat and free energy of formation respectively of the activated complex, k' and h are Boltzmann's and Planck's constants respectively. Over a small range of temperatures this equation can be written

$$k = B \exp(-\Delta H^\ddagger/RT) \quad 3.$$

$$\text{where } B = (k'T/h) \exp(\Delta S^\ddagger/R).$$

The present state of knowledge concerning the rate of mass transfer between two liquids will now be discussed in more detail, thus providing the context for the present work. First, the several theories of the kinetics of mass transfer will be reviewed (1.2.2 and 1.2.3), then the observations concerning the influence of three surface phenomena on the kinetics will be described, and finally the influence of a chemical reaction at or near the interface will be considered.

1.2 Kinetics of mass transfer between two fluid phases

1.2.1 Nomenclature

A	=	Interfacial Area, cm ²
C	=	Concentration, g mol litre ⁻¹
D	=	Diffusion coefficient, cm ² sec ⁻¹
g	=	Acceleration due to gravity, cm sec ⁻²
j	=	Transfer rate, g mol sec ⁻¹ cm ⁻²
k	=	Individual mass transfer coefficient, cm sec ⁻¹
K	=	Overall " " " " "
L	=	Length of stirrer, cm.
m	=	Distribution coefficient
N	=	Stirring rate, rev. sec ⁻¹
s	=	Danckwerts surface renewal factor
θ	=	Age of a surface element
\bar{x}	=	Effective film thickness, cm.
V	=	Volume, cm ³
γ	=	Surface or Interfacial Tension, dyne cm ⁻¹
ν	=	Kinematic viscosity, cm ² sec ⁻¹
η	=	Viscosity g sec ⁻¹ cm ⁻¹
ρ	=	Density g cm ⁻³

Subscripts α & β refer to individual phases
 i = interfacial conditions
 org, o, s = organic phase
 aqu, a, w = aqueous phase
 Superscript * = equilibrium conditions

Dimensionless Groups

Re = Reynolds number $LN \rho / \eta$
 Sc = Schmidt Group η / D

1.2.2 Two-Film theory

This was the first fundamental theory of mass transfer; it was proposed by Hatta²² and Lewis and Whitman²³ & ²⁴, and was based on the general boundary layer theory of Nernst²⁵ & ²⁶. In this theory it is assumed that the bulk of each phase is of uniform concentration, C_α and C_β respectively, and that on either side of the interface there is a boundary layer of non-uniform concentration. The transfer across the boundary layer is by molecular diffusion only and hence the rate of transfer obeys Fick's laws of diffusion. It is also assumed that there is equilibrium across the interface, i.e. there is no interfacial resistance, and hence $C_{\beta i} / C_{\alpha i} = m$. Fick's second law of diffusion, when applied to this system, becomes:-

$$dc/dt = Dd^2c/dx^2 \quad 4.$$

where it is assumed that D is independent of concentration. When a steady state is reached, equation 4 reduces to:-

$$Dd^2c/dx^2 = 0 \quad 4a.$$

Then integration with the conditions

$$C = C_{\alpha i} \text{ at } x=0$$

$$\text{and } C = C_\alpha \text{ at } x = x_\alpha$$

$$\text{leads to:- } C_{\alpha x} = x(C_\alpha - C_{\alpha i})/x_\alpha + C_{\alpha i} \quad 5.$$

From this, differentiation gives:-

$$dc/dx = (C_\alpha - C_{\alpha i})/x_\alpha \quad 6.$$

By Fick's first law, for transfer from bulk α

$$j = D_{\alpha} (dc/dx)_{x=0} \quad 7.$$

$$\text{Therefore } j = D_{\alpha} (C_{\alpha} - C_{\alpha i}) / x_{\alpha} \quad 8.$$

Similarly, at steady state, with no mass build-up at the interface

$$j = D_{\beta} (C_{\beta i} - C_{\beta}) / x_{\beta} \quad 9.$$

The individual mass transfer coefficients k_{α} and k_{β} are defined by

$$j = k_{\alpha} (C_{\alpha} - C_{\alpha i}) \quad 10.$$

$$\text{and } j = k_{\beta} (C_{\beta i} - C_{\beta}) \quad 11.$$

and therefore, for the two film theory, the values of k_{α} and k_{β} are given by D_{α} / x_{α} and D_{β} / x_{β} respectively.

In practice, measurement of interfacial concentration is impossible, and further mass transfer coefficients are defined in terms of bulk concentrations only. These are the overall mass transfer coefficients K_{α} and K_{β} and are defined by the equations

$$j = K_{\alpha} (C_{\alpha} - C_{\alpha}^{\#}) \quad 12.$$

$$\text{and } j = K_{\beta} (C_{\beta}^{\#} - C_{\beta}) \quad 13.$$

$$\text{where } C_{\alpha}^{\#} = C_{\beta} / m \quad 14.$$

$$\text{and } C_{\beta}^{\#} = m C_{\alpha} \quad 15.$$

From these definitions, and assuming interfacial equilibrium, a relationship between individual and overall mass transfer coefficients can be derived as follows:-

$$\text{since } j = k_{\alpha} (C_{\alpha} - C_{\alpha i}) = k_{\beta} (C_{\beta i} - C_{\beta}) \quad 16.$$

$$\text{then } j/k_{\alpha} = C_{\alpha} - C_{\alpha i} \quad 17.$$

$$\text{and } j/k_{\beta} = C_{\beta i} - C_{\beta} \quad 18.$$

which, when combined with (12) or (13) and $C_{\beta i} / C_{\alpha i} = m$, leads to

$$1/K_{\alpha} = 1/k_{\alpha} + 1/m k_{\beta} = 1/m K_{\beta} \quad 19.$$

If m is large and k_α and k_β are similar in value

$$\text{then } 1/K_\alpha = 1/k_\alpha \quad 20.$$

An analogy can be made between mass transfer coefficient and electrical conductivity since the latter is defined as the rate of electrical flow per unit area per unit potential gradient. The various stages in the transfer correspond to simple resistances in series and the rate constants k are equivalent to the conductance of each resistance. Using this analogy it is simple to adapt (19) to take into account the presence of an interfacial resistance, the result is

$$1/K_\alpha = 1/k_\alpha + 1/mk_\beta + 1/k_i \quad 21.$$

where k_i is the interfacial mass transfer coefficient.

It should be noted that equations 19-21 are dependent only on the definition of mass transfer coefficient and not on the assumption of any particular theory of mass transfer. Recent work by Gordon and Sherwood²⁷, Searle and Gordon²⁸ and Lewis²⁹ uphold this concept of reciprocal additivity of mass transfer coefficients.

1.2.3 Surface Renewal Theories

The basic "two-film" theory forms a good basis for correlating experimental results in mass transfer. However, there are instances where the theory departs from experimental results. Higbie³⁰ studied the absorption of carbon dioxide into water during short contact times and found that the rate of transfer decreased with increasing contact time and approached a steady value. Higbie suggests that turbulence existed right up to the interface and that elements of the interface were renewed from the bulk phase before a steady state was reached.

36-37

Dankwerts³¹⁻³⁵ and Kishinevskij³⁶⁻³⁷ have developed these ideas and an outline of Dankwerts' theory is as follows:-

The interface can be considered to be made up of many elements of area, from or into which transfer takes place by unsteady state diffusion. These elements are being

continually replaced by new elements coming from the bulk of the solution due to the stirring of the system. The depth of penetration of concentration gradient is less than the film thickness postulated by Lewis²³ and Whitman²⁴, thus elements do not reach a steady state of transfer. Other considerations were: the chance of any element of surface being replaced is independent of the age of the element and the fraction of the surface replaced in unit time s is dependent on the hydrodynamics of the system.

Solution of the Fick's law equation ,

$$dC/d\theta = Dd^2C/dx^2 \quad 22.$$

for a surface element of age θ , with boundary conditions

$$\begin{aligned} \theta = 0 & \quad C = C_\beta \\ \theta > 0 & \quad x = 0 \quad C = C_{\beta i} \\ & \quad x \rightarrow \infty \quad C = C_\beta \end{aligned}$$

gives the rate of transfer per unit area $\psi(\theta)$ as

$$\psi(\theta) = (C_{\beta i} - C_\beta) (D/\pi\theta)^{\frac{1}{2}} \quad 23.$$

Hence, for a stagnant liquid, in which there is no surface renewal, the rate of transfer decreases rapidly after contact between the two phases is made.

In a stirred system in which a significant fraction of the surface is replaced in unit time, a steady state will be obtained for the system as a whole, although locally there is no steady state. Under overall steady state conditions the fraction of surface elements of ages between θ and $(\theta + d\theta)$ will be constant. If this fraction is given by $\rho(\theta) \cdot d\theta$ it is also equal to the fraction of elements entering the age-group θ to $(\theta + d\theta)$ from the age group $(\theta - d\theta)$ to θ in a time $d\theta$, less that portion which is replaced by fresh surface in time $d\theta$. Thus

$$\rho(\theta)d\theta = \rho(\theta - d\theta) d\theta(1 - sd\theta) \quad 24.$$

which can be written as

$$\rho(\theta) = \rho(\theta) - [d\rho/d\theta]d\theta - s\rho(\theta) d\theta \quad 25.$$

hence

$$d\delta / d\theta = -s\delta \quad 26.$$

now

$$\int_0^{\infty} \delta \, d\theta = 1 \quad 27.$$

which, after integration of (26), leads to

$$\delta = s \exp(-s\theta) \quad 28.$$

The rate of absorption ψ_0 into those elements of age θ and of fractional area $s[\exp(-s\theta)]d\theta$ is obtained from (23) and is given by

$$\psi_0 = (C_{\beta i} - C_{\beta}) s [\exp(-s\theta)] \left[D/\pi\theta \right]^{1/2} d\theta \quad 29.$$

Hence, the mean rate of absorption over the whole surface area is given by the equation:-

$$j = (C_{\beta i} - C_{\beta}) \left[D/\pi \right]^{1/2} \int_0^{\infty} s [\exp(-s\theta)] / \theta^{1/2} d\theta \quad 30.$$

$$\text{Hence } j = (C_{\beta i} - C_{\beta}) (Ds)^{1/2} \quad 31.$$

$$\text{Therefore } k_{\beta} = (Ds)^{1/2} \quad 32.$$

This should be compared with the relationship found in the two-film theory, viz:-

$$k_{\beta} = D/x_{\beta} \quad 33.$$

With this theory, as with the two-film theory, the overall mass transfer coefficient can be found from the individual phase mass transfer coefficients and the interfacial mass transfer coefficient.

The transfer of solutes between unstirred solutions has been considered by a number of workers³⁸⁻⁴³; exact unsteady state solutions of Fick's equations being obtained. However, these results have little significance for stirred systems, where the bulk of each phase is homogeneous. However, various modifications of the two-film theory and the surface renewal theory have been made to help correlate experimental results.

Potter⁴⁴ claims that Danckwerts theory has a very limited use due to the difficulty in allocating a value to \bar{s} . He has

considered the basic boundary layer theory for heat transfer and, by developing analogies with mass transfer, has evolved equations for transfer between moving boundary layers. His basic results are given by:-

$$k_a = (D_a/x_a) (\eta_a/\rho_a D_a)^p (U_a x_a/\nu_a)^{\frac{1}{2}} \phi [U_\beta \eta_\beta \rho_\beta / U_a \eta_a \rho_a] \quad 34.$$

where $U_{\alpha,\beta}$ is the velocity outside the boundary layer

ϕ is a function

ρ is a function of U_β/U_a and $\eta_\beta \rho_\beta / \eta_a \rho_a$

and other symbols are the same as given in the nomenclature (page 10). This formula seems to have little advantage over either of the earlier formulae because there are more indeterminate variables.

Toor and Marchello⁴⁵ have claimed that the two-film and surface-renewal theories are complementary and are the limiting cases for laminar and turbulent flows. With laminar flow the surface renewal factor \underline{s} is zero, but with turbulent flow the undisturbed layer is thin or non-existent, so the surface renewal factor becomes significant.

Considering the surface elements of Dankwerts theory, elements having a short life in the surface will not reach a steady state, whereas elements with a long surface life will reach this state. If all the elements are considered to be bounded in a region between a plane of distance \underline{L}' from the interface and the interface itself, the boundary conditions for an element of age $\underline{\theta}$ are

$$\begin{aligned} \theta = 0 \quad x > 0 \quad C &= C_\beta \\ \theta > 0 \quad x = 0 \quad C &= C_{\beta i} \\ \theta > 0 \quad x > L' \quad C &= C_\beta \end{aligned}$$

The instantaneous solution of the diffusion equation (23) is given by

$$\psi(\theta) = (C_{\beta i} - C_\beta) (D/\pi\theta)^{\frac{1}{2}} \left[1 + 2 \sum_{n=1}^{\infty} \exp(-n^2 L'^2/D\theta) \right] \quad 35.$$

and the mean rate for the whole area is given by

$$j = \int_0^{\infty} \underline{s} [\exp(-s\theta)] \psi(\theta) d\theta \quad 36.$$

This is conveniently expressed as

$$j = (C_{\beta i} - C_\beta) (Ds)^{\frac{1}{2}} \coth \left[L' (s/D)^{\frac{1}{2}} \right] \quad 37.$$

If $s \gg D/L'^2$, which may be possible in turbulent flow,

$$j = (C_{\beta i} - C_{\beta}) (Ds)^{\frac{1}{2}} \quad 38.$$

which is the result obtained from the penetration theory.

If $s \ll D/L'^2$ which is consistent with laminar flow then

$$j = (C_{\beta i} - C_{\beta}) D/L' \quad 39.$$

which is the result obtained from the two-film theory. Hence, both the surface renewal (penetration) and the two-film theories apply in the limiting cases.

In a later publication, Toor and Marchello⁴⁶ have modified this theory and proposed an internal mixing model in which low level turbulence near the phase boundary causes only local mixing. The mathematical treatment of this model is complex but the final result is:-

$$j = (C_{\beta i} - C_{\beta}) \left[(Ds)^{\frac{1}{2}}/2 \right] \left[\left\{ 1 + \cosh (L'(s/D)^{\frac{1}{2}}) / \sinh (L'(s/D)^{\frac{1}{2}}) \right\} \right] \quad 40.$$

this reduces to:-

for turbulent flow ($s \gg D/L'^2$)

$$j = (C_{\beta i} - C_{\beta}) (Ds)^{\frac{1}{2}}/2 \quad 41.$$

for laminar flow ($s \ll D/L'^2$)

$$j = (C_{\beta i} - C_{\beta}) D/L' \quad 42.$$

The factor of two difference between (38) and (41), for the first limit, is due to the driving force being considered as $(C_{\beta i} - C_m)$, where C_m is the average concentration in the mixing zone, i.e. $(C_{\beta i} + C_{\beta})/2$.

Therefore, $(C_{\beta i} - C_m) = (C_{\beta i} - C_{\beta})/2$. In both of Toor and Marchello's theories the surface renewal and two-film concepts are limiting cases of a region in which both types of transfer play a part.

Shappel⁴⁷ also concluded that molecular diffusion was important at low Reynolds numbers and eddy diffusion at high Reynolds numbers.

It should be noted that in all the theories so far proposed fluid velocity gradients have been neglected. The

complete diffusion equation in one dimension is:-

$$\frac{dC}{dt} + v_x \frac{dC}{dx} = D \frac{d^2C}{dx^2}$$

43.

where v_x is the velocity in the x direction.

The overall driving force in mass transfer is generally taken to be the effective concentration gradient between the two phases, but Hennico and Vermeulen⁴⁸ suggested that the activity gradient is the more realistic parameter. However, although this is the more correct approach, the concept is of limited use, since the activity data are rarely available.

The choice of a mathematical relationship to describe mass transfer would seem to depend on the nature of the fluid flow occurring and special consideration must be taken of the hydrodynamics involved in the system being studied.

1.2.4 Interfacial Turbulence

Interfacial turbulence may arise from two sources:-

- (a) That brought about by the bulk instability caused by excessive stirring of the bulk phases or high temperature gradients.
- (b) Spontaneous interfacial turbulence of a localised nature, for instance that caused by the Marangoni effect which originates from local concentration gradients near to the interface.

Interfacial turbulence will affect mass transfer in a variety of ways. Bulk interfacial turbulence will cause variations in the interfacial area as well as changes in the degree of surface renewal at the interface. Spontaneous interfacial turbulence will cause local and short time variation in the rate of mass transfer, due to temporary high concentration gradients. This phenomenon of spontaneous interfacial turbulence can lead to interfacial eruptions and in extreme cases spontaneous phase mixing. Haydon and Davis^{49,50} have proposed that surface renewal accounts for these local changes in surface concentration and hence interfacial tension, and on this basis they derived the formula

$$\Delta \gamma = m C_x (1 + m) \left[\frac{d\gamma}{dC} \right]_{C = C_x}$$

44.

where $\Delta \gamma$ is the difference between the interfacial tension of an element and that of its surroundings.

It was assumed that the solute from one surface element is distributed between equal volumes on either side of the interface. They also calculated the energy acquired by a drop,

due to local turbulence, and the resulting drop movement, which is in the pattern of a damped harmonic oscillation. In another series of experiments Haydon⁵¹ measured the rise of a drop of isobutanol in water caused by squirting acetone at the drop. He predicted that:-

$$M (\partial C / \partial \gamma) = AC / gh (1 + m)$$

45.

where h is the height of drop rise, A the area of altered interfacial tension, M the relative drop weight and C the solute concentration. By projecting the image of the drop on a screen, the amount squirted could be adjusted to give a constant height of drop rise for different concentrations of solute. Plotting $M / (\partial \gamma / \partial C)$ against $C / (1 + m)$ showed that the area of interfacial tension change, for the systems chosen, was fairly constant; however, in the presence of a detergent, A was apparently reduced. Sternling and Scriven⁵² have deduced a mathematical equation relating the derivation of interfacial energy and the resulting instability. They predict that interfacial turbulence will be most likely to occur if at least some of the following conditions are present:-

- (a) Solute is being transferred out of the phase of higher viscosity.
- (b) Solute is being transferred from the phase of lower diffusivity.
- (c) There is a large difference in kinematic viscosity and solute diffusivity in the two phases.
- (d) There are steep concentration gradients occurring near the interface.
- (e) The interfacial tension is sensitive to solute concentration. This must always occur.
- (f) There is a low viscosity and diffusivity in both phases.
- (g) Other surface active agents are absent.
- (h) There is a large interfacial area-volume ratio.
- (i) There are high solute concentrations.

Further experimental and photographic evidence for this effect has been provided by Goltz⁵³, Garner, Nutt and Mohtadi⁵⁴, Groothuis and Zinderweg⁵⁵ and others; mostly with reference to

suspended drops. Evidence is also available for this phenomenon at flat interfaces. Grootius et al⁵⁵ have shown that the direction of transfer affects the degree of turbulence and spontaneous mixing. This accounts for the dependence of extraction rate in a spray column on the phase which is continuous, as spontaneous dispersion of one can reduce drop coalescence. This effect was also noted by Johnson and Bliss⁵⁶ and a similar effect was noted by Pratt, Gayler, Murdock, Thornton and Smith⁵⁷⁻⁵⁹, with packed columns and rotating disc contactors. In systems in which spontaneous interfacial turbulence occurs, it is almost impossible to predict quantitatively the effect it will have upon the rate of mass transfer, and hence every effort should be made to prevent its occurrence in transfer rate measurements.

1.2.5 The Influence of Surfactants

Surface active agents affect the rate of mass transfer in two ways, depending on the nature of the surfactant present. Some surfactants appear to prevent the occurrence of interfacial turbulence and hence reduce the rate of mass transfer. Others form polymolecular membranes at the interface and hence cause definite interfacial resistances. Melhus, Terjesen, Lindland and Boye-Christiansen⁶⁰⁻⁶⁴ studied the effect of teepol and other surfactants on the rate of transfer of iodine and nitrophenol from water into drops of carbon tetrachloride. They also studied the effect of the surfactants on interfacial tension for the same systems. From a comparison of the relationships between concentration of surfactant C_s , interfacial resistance and interfacial tension, for strongly adsorbed surfactants, they derived the following correlations:-

$$C_s = KA_o f / (1 + A_o f)^n \quad 46.$$

$$\text{and } C_s = K_1 R_i / (1 - K_2 R_i)^{0-1} \quad 47.$$

where $A_o f$ is the proportion of the surface covered by adsorbed molecules and R_i the coefficient of interfacial resistance. From these relationships, Melhus et al⁶⁰⁻⁶⁴ postulated that the only correlation is that between the interfacial resistance and the fraction of the interfacial area covered by surfactant film. It should be noted that imperfections in this correlation can be related to the fact that, in studying the rate of mass transfer to falling drops, there is probably insufficient time given for the attainment of adsorption equilibrium. Except at very low concentrations of surfactant, they found no difference between iodine and nitrophenol in the relationships they produced between fractional surface coverage and interfacial resistance to mass transfer. From these results they deduced that the action of

these surfactive agents was hydrodynamic in nature, i.e. they reduced the degree of spontaneous interfacial turbulence.

In a further set of experiments, Melhus et al⁶⁰⁻⁶⁴ concluded that only strongly adsorbed surfactants obey the above isotherms. They found that weakly adsorbed surfactants obeyed the Langmuir isotherm and that in the presence of high concentrations of these surfactants the reduction in mass transfer rate tended to a constant value which was independent of the nature and concentrations of the surfactant. They also concluded that, in the presence of high concentrations of surfactant, the rate of mass transfer was equivalent to that for transfer from a solid sphere, i.e. the surfactant was reducing interfacial turbulence and surface renewal to a negligible value.

Using a system of two independently stirred phases with a static interface (similar to the one used in the work to be described), Gordon and Sherwood²⁷ found that surfactants had little effect on the mass transfer coefficient. However, Lewis⁶⁵⁻⁶⁶, using a similar experimental arrangement, found that a reduction in transfer rate occurred in the presence of a rigid protein film at the interface. Davis and Wiggill⁶⁷ suggested that this was due to the formation of polymeric complexes between the surfactant and traces of metal ions from the cell Lewis was using. These complexes caused a resistance similar to that found by themselves in the presence of sorbiton tetrastearate in an unstirred system. Meyer⁶⁸ also studied the effect of surfactants in a stirred cell with static interface and concluded that the effect was largely hydrodynamic in nature, i.e. the surfactant reduced the interfacial turbulence. He also concluded that, in the presence of an incompressible monolayer, the hydrodynamic effect was more than a reduction in interfacial turbulence. He postulated that a change was occurring in the mode of transfer to one which was controlled by molecular diffusion through a film; whereas, in the absence of surfactants, surface renewal predominated.

No firm conclusions can be drawn as to the precise effect of surfactants. It would appear to depend on the design of the extraction vessel, the system being studied and the type and concentration of surfactant. However, it would seem that weak surfactants reduce the interfacial turbulence, whereas strong surfactants, particularly those producing a solid-like film, have a more profound effect. The effect of surfactants on the rate of mass transfer is of particular importance in the work to be described, since both the organic extracting agents and the organo-metallic complexes are of themselves surface active agents. The organo-metallic compounds may well form

polymeric surface complexes. However, in the stripping reactions studied, the conditions at the interface would make these complexes unstable. The surface active nature of the extracting agents may well be advantageous in reducing spontaneous interfacial turbulence, which would otherwise make the analysis of kinetic data more difficult.

1.2.6 Interfacial Resistance

In systems where mass transfer occurs without chemical reaction, the presence or otherwise of an interfacial resistance is not very certain. No reference has been found to a large reduction in mass transfer rate, below that predicted hydrodynamically, other than in those systems where surface active agents play a considerable part. The measurement of small interfacial resistances is extremely difficult, in view of (a) the limits of reproducibility of mass transfer rate determination set by the effects of interfacial turbulence and surfactants, and (b) the difficulty of distinguishing between interfacial resistance and bulk phase resistance.

Apart from the effect of the presence of surfactants, interfacial resistance without chemical reaction may be due to two factors:

- (i) The rate of exchange of the solvation layer of the species being extracted. This may be considered to be equivalent to the rate of formation of an activated complex.
- (ii) The effect of steric hindrance. For example, the degree of hydrogen bonding in the system may affect the orientation of the species at the interface. Sinfelt⁶⁹ and Sinfelt and Drickamer^{70,86} used this factor to explain the variation in the interfacial resistance for the transfer of sulphur dioxide between n-heptane and a variety of organic solvents. From the results there appeared to be a correlation between the degree of hydrogen-bonding involved in a system and the interfacial resistance.

The authors considered that the degree of hydrogen-bonding would affect the orientation of the species and that certain preferred orientations would reduce the resistance to motion through the interface. This idea was developed in terms of an energy barrier at the interface (i.e. an energy of orientation).

The other main cause of an interfacial resistance is a slow chemical reaction. This will be covered in the section to follow.

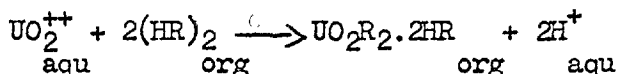
1.2.7 Mass Transfer with Chemical Reaction

Mass transfer with chemical reaction can be divided into two broad classes:

- (a) That in which appreciable mass transfer of one or more of the reactants across the interface takes place in the absence of the other reactants. In this case the reaction takes place within one or other of the phases and not at the interface.
- (b) That in which the two reactants are in different phases and no transfer is possible without reaction taking place. The reaction must therefore take place at the interface.

In the first case the reaction alters both the distribution of solute between the phases and the rate of transfer. A good example of this is the absorption of carbon dioxide into sodium hydroxide solution. Carbon dioxide can be absorbed by water, an equilibrium being set up between the partial pressure of carbon dioxide in the gas phase and its concentration in the aqueous phase. If sodium hydroxide is present in the aqueous phase, the carbon dioxide reacts with it in the boundary layer and the equilibrium extraction is increased in favour of the water phase. The rate of absorption is also affected by this reaction.

An example of the second class of reaction is the transfer of uranium into di-2-ethylhexyl-phosphoric acid in paraffin. The interfacial reaction is:-



(where R is the organo-phosphate radical). In the absence of this reaction, transfer of uranium into the organic phase is negligible since simple uranyl salts have a very low solubility in paraffin.

Both these classes of transfer can be divided into two types:- the type in which the chemical reaction is slow and hence rate determining, and the type in which the chemical reaction is fast by comparison with the rate of mass transfer.

Some of the earliest work on the effect of chemical reaction was that conducted by Hatta⁷³ on the absorption of carbon dioxide by potassium hydroxide. Interpreting his results in terms of the Whitman two-film theory, he proposed the following equation for the rate of absorption into water:-

$$1/K = H/k_g + 1/k_L \quad 48.$$

where K is the overall mass transfer coefficient, with respect to the liquid phase, k_g and k_L are the gas and liquid phase film coefficients respectively, and H is the gas solubility coefficient (similar to the partition coefficient m). This equation is another example of the additivity concept and can be compared with equation 19. When the water phase was replaced by potassium hydroxide solution, which reacts instantaneously with the carbon dioxide, the liquid phase film coefficient increased according to the equation

$$k'_L = k_L (1 + D_{KOH} C_{KOH} / 2DCO_2 C_{iCO_2}) \quad 49.$$

where k'_L is the new film coefficient and k_L is the film coefficient in the absence of potassium hydroxide. As carbon dioxide is a sparingly soluble gas ($H \ll 1$), H/k_g is small compared with $1/K$ and therefore

$$1/K \approx 1/k'_L \quad \text{and} \quad C_{iCO_2} = H P_{CO_2} \quad 50.$$

For highly soluble cases $1/K = H/k_g$ and hence the chemical reaction has little effect on the rate of mass transfer. Hatta⁷³ then extended this work to the absorption of carbon dioxide by potassium carbonate solutions. In this process the reaction is not very fast and the liquid phase coefficient is defined by:-

$$k'_L = \beta k_L \quad 51(a).$$

where β is given by:-

$$\beta = \gamma / \tanh \gamma \quad 51(b).$$

and γ is given by:-

$$\gamma = (k_c D_{CO_2})^{1/2} / k_L \quad 51(c).$$

where k_c is the first order rate constant, with respect to carbon dioxide concentration, for the reaction between carbon dioxide and potassium carbonate. If k_c is small, $\gamma < 0.2$, then k'_L is

equal to k_L . If k_c is large, $\gamma > 3$, then β is approximately equal to γ and k'_L is given by

$$k'_L = (k_c D_{CO_2})^{\frac{1}{2}} \quad 51(d)$$

Dankwerts³¹ also studied the effect of instantaneous chemical reaction in terms of the penetration theory and developed the following equations for the liquid film coefficients. In the absence of chemical reaction

$$k_L = (Ds)^{\frac{1}{2}} \quad 32.$$

(see page 14). In the presence of an instantaneous first order chemical reaction

$$k'_L = k_L / \text{erf} \left[\beta / D^{\frac{1}{2}} \right] \quad 52,$$

where β is defined by the equation

$$(C_i / D_R^{\frac{1}{2}}) (\exp \beta^2 / D_R) (1 - \text{erf} \beta / D_R^{\frac{1}{2}}) = (C_R / D^{\frac{1}{2}}) (\exp \beta^2 / D) (\text{erf} \beta / D^{\frac{1}{2}}) \quad 53.$$

where C_i is the interfacial concentration of solute; D is the diffusion coefficient of the absorbed species, D_R is the diffusion coefficient of the reacting species and C_R is the bulk concentration of this reacting species. If $D = D_R$ then the equation simplifies to:-

$$k'_L = k_L (C_i + C_R) / C_i \quad 54.$$

Dankwerts, however, makes no attempt to obtain solutions for slow chemical reactions, though in the extreme the result is the same as that in the absence of a reaction.

Sherwood and Wei⁷⁴ have modified Hatta's equations relating the effect of an instantaneous chemical reaction on the individual film coefficient and have derived the more general equation

$$k'_L = k_L \left[1 + (r D_\beta / D_\alpha)^n C_\beta / C_{\alpha i} \right] \quad 55.$$

where α is the transferring solute and β the reacting solute, r is the number of moles of α reacting with 1 mole of β and $n = 1$ for the film theory and 0.5 for the penetration theory. This relationship was examined by studying the rate of transfer of

acetic acid dissolved in benzene, into sodium hydroxide. If k'_L and k_o are the individual phase mass transfer coefficients for the aqueous and organic phases respectively, K_L the overall mass transfer coefficient and m the distribution coefficient, then by the concept of additivity of resistances

$$1/K_L = 1/mk_o + 1/k'_L \quad 56.$$

This relationship predicts that when $C_\beta = 0$

$$1/K_L = 1/mk_o + 1/k_L \quad 58.$$

and that as C_β increases the value of $1/K_L$ tends to a constant value of $1/mk_o$. However, experimental results showed that as C_β increased, the value of K_L rose to a maximum value greater than mk_o and then dropped again. It was thought that two factors were responsible for this deviation from theory:

- (a) Interfacial turbulence was occurring.
- (b) Some of the saponification was taking place in the organic phase.

28

Searle and Gordon also studied this system using the equation in the form

$$(k'_L/k_L) - 1 = (r D_\beta/D_\alpha)^n C_\beta/C_{\alpha i} \quad 59.$$

They found that taking n as 1 or 0.5 made little difference to the elucidation of the results. They did find, however, that the results correlated better with an equation of the form

$$(k'_L/k_L) - 1 = (r D_\beta/D_\alpha)^n C_\beta^q/C_{\alpha i} \quad 60.$$

where q was between 1.3 and 1.5 for this system. It was thought that this was due partly to the fact that sodium hydroxide diffuses as ions rather than as a molecular species.

These difficulties of obtaining exact solutions for individual mass transfer coefficients in this type of system are similar to the difficulty in obtaining exact mathematical equations to predict the rate of transfer of a single solute. The mechanism is far from certain and depends to a great extent on the system being studied and the method of extraction.

The systems which were studied experimentally, and reported later in this thesis, were of the class in which the chemical reaction must take place at the interface. The effect

of an interfacial reaction has not been investigated theoretically before. However, the problem is capable of simple solution along the following lines.

First, consider the system in which there is a rapid interfacial reaction of the type



The bulk concentrations are C_A , C_B , C_C and C_D , and the interfacial concentrations are C_{Ai} , C_{Bi} , C_{Ci} , C_{Di} . It will be assumed there is no interfacial resistance, which is consistent with a rapid interfacial reaction, and hence the species being transferred are in equilibrium at the interface. This fact is expressed in the equation

$$H = (C_{Ci} \times C_{Di}) / (C_{Ai} \times C_{Bi}) \quad 62.$$

where H is the equilibrium constant. It is convenient (and consistent with the experimental work to be described) to consider the case in which species B and C are present in excess so that their concentrations do not change appreciably. The distribution coefficient m is given by

$$m = C_D / C_A^* \quad 63.$$

where C_A^* is the concentration of A in equilibrium with C_D and is defined by

$$C_A^* = C_D \times C_C / H C_B \quad 63a.$$

If k_A , k_B , k_C and k_D are the individual mass transfer coefficients and $\overline{k_A}$ is the overall mass transfer coefficient, then j , the rate of mass transfer in the direction aqueous to organic, is given by the equations

$$j = k_A (C_A - C_{Ai}) \quad 64.$$

$$= k_B (C_B - C_{Bi}) \quad 65.$$

$$= k_C (C_{Ci} - C_C) \quad 66.$$

$$= k_D (C_{Di} - C_D) \quad 67.$$

$$= K_A (C_A - C_A^*) = K_A (C_A - C_D / m) \quad 68.$$

Rearrangement and substitution in 62 gives

$$\begin{aligned} H \left[\frac{C_A}{K_A} - \frac{(C_A - C_A^*)}{k_A} \right] \left[\frac{C_B}{K_A} - \frac{(C_A - C_A^*)}{k_B} \right] \\ = \left[\frac{C_C}{K_A} + \frac{(C_A - C_A^*)}{k_C} \right] \left[\frac{C_D}{K_A} + \frac{(C_A - C_A^*)}{k_D} \right] \end{aligned} \quad 69.$$

With C_C and C_B large, (69) reduces to

$$1/K_A = 1/k_A + 1/mk_D \quad 70.$$

which is similar to that for transfer of a single solute, and indicates that the rate is controlled by the transfer of the less concentrated species A and D as expected. This result is based solely on a first order relationship between the rate of transfer and the concentration gradient for each species, and is not dependent on the mechanism of transfer. In many of the systems studied, in the experimental work reported later in this thesis, the concentrations represented by C_B and C_C in the above formula are not sufficiently large to use the simplified form (70) although they are either in excess or maintained at a controlled level throughout extraction. In this event the relationship for K_A is more complex and dependent on the concentrations of all the species present, and the rate j will not follow an exact first order relationship with respect to C_A . A full analysis of this effect will be made when these particular systems are studied.

When the reaction at the interface is slow, rather than instantaneous, the solutions at the interface are no longer in equilibrium and there is effectively an interfacial resistance. If j' is the overall rate of transfer, j is the rate of transfer in the absence of any interfacial resistance, j_C the rate of transfer in the presence of an interfacial resistance alone, F the driving force and R' , R and R_C the appropriate resistances, then

$$j' = F/R', \quad j = F/R \quad \text{and} \quad j_C = F/R_C \quad 71.$$

Using the concept of additivity of resistances in series, in which case

$$R + R_C = R' \quad 72.$$

$$\text{then} \quad 1/j' = 1/j + 1/j_C \quad 73.$$

If K'_A and K_A are the overall mass transfer coefficients for the transfer of A with and without interfacial resistance respectively and K_C is the rate constant of an interfacial reaction n^{th} order with respect to A , then

$$1/K'_A (C_A - C_A^{\text{II}}) = 1/K_A (C_A - C_A^{\text{II}}) + 1/K_C (C_A^{\text{II}} - C_A^{\text{I}*}) \quad 74.$$

In the simplest case with n equal to 1, 74 reduces to

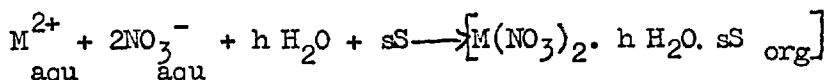
$$1/K'_A = 1/K_A + 1/K_C \quad 75.$$

when K_A is large compared with K_C then

$$1/K'_A = 1/K_C \quad 76.$$

i.e. the rate of transfer is determined entirely by the rate of the interfacial reaction and the concentration gradients, between the bulk of the solutions and the interface, are negligible.

Attempts to measure the values of K_C for systems are few. Lewis²⁹ studied the rate of transfer of uranyl nitrate between aqueous solutions and tributyl phosphate and obtained values of K'_C for this system using calculated values of K_A . He found that a definite interfacial resistance existed, which appeared to increase with time. He attributed this to a decrease in interfacial turbulence and a relaxation of unsteady state diffusion. McManamey⁷⁵ studied the extraction of nickel, copper and cobalt nitrates from aqueous solutions into n-butanol, using a similar technique for calculating the interfacial mass transfer coefficients to that used by Lewis. He found that the three nitrates considered gave similar interfacial resistances, which were considerably higher than that found by Lewis for the uranyl nitrate system. No time effect was found and the results appeared to be consistent with a reaction



where S denotes solvent molecules. Keisch⁷⁶ attempted to obviate this problem of measurement of interfacial resistance in the presence of bulk phase resistance, by using a specially designed micro-cell, in which the stirrers could be rotated at high speeds in each half of the cell without disrupting the interface. He used this cell to study the transfer of uranyl nitrate from nitric acid solutions into tributyl phosphate in an organic diluent. He studied the rate by using an isotopic exchange technique in which the two phases were always at bulk chemical equilibrium. This method has two advantages: first, it eliminates spontaneous interfacial turbulence (the Marangoni effect) and, secondly, it can be shown mathematically that the rate of exchange of the isotopic species is always first order with respect to the concentration of isotope present. He found that, over the range of stirrer speeds investigated (2,000-3,000 r.p.m.), the rate

of transfer was independent of stirring speed and hence he assumed that the rate of transfer was chemically controlled. At 25°C the rate could be represented by the following equation:

$$R = K \left[\text{UO}_2^{++} \right]_{\text{aq}} \left[\text{NO}_3^- \right]_{\text{aq}}^{1.2} \left[\text{TBP} \right]_{\text{org}}^{1.8}$$

77.

the hydrogen ion concentration having no effect on the rate. From this rate equation, he postulated the following reaction path:

- (i) $\text{UO}_2^{++} + \text{NO}_3^- \xrightleftharpoons{K_1} \text{UO}_2(\text{NO}_3)^+$ fast
- (ii) $\text{UO}_2(\text{NO}_3)^+ + \text{TBP} \xrightleftharpoons{K_2} \text{UO}_2(\text{NO}_3)^+ \text{TBP}$ fast
- (iii) $\text{UO}_2(\text{NO}_3)^+ \text{TBP} + \text{TBP} \xrightleftharpoons{k_1} \text{UO}_2(\text{NO}_3)^+ \cdot 2 \text{TBP}$. slow
- (iv) $\text{UO}_2(\text{NO}_3)^+ \cdot 2 \text{TBP} + \text{NO}_3^- \xrightleftharpoons{k_2} \text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{TBP}$ fast.

This gives an overall rate equation of

$$R = k_1 K_1 K_2 \left[\text{UO}_2^{++} \right] \left[\text{NO}_3^- \right] \left[\text{TBP} \right]^2$$

78.

At 6°C and 45°C the experimental rate equation differed in the values of the indices and he proposed that this was due to changes in the relative rates of the various stages.

It should be noted that, although the stirrer speeds were high, the Reynolds numbers were of the same order as those obtained in Lewis' and McManamey's work, as also were the transfer rates. In view of their findings it is doubtful whether Keisch's assumption that the transfer was entirely chemically controlled is valid. Chester⁷⁷ also claimed that the results could be interpreted in terms of diffusion control. He proposed that the observation that the rate was independent of stirrer speed was fortuitous; i.e. the change of stirrer speed was balanced by a change in interfacial area. However, it is difficult to accept that an increase in stirrer speed could cause a decrease in interfacial area. The cell being made entirely of metal, no observation of the interface during transfer was possible.

In the work of both Lewis²⁹ and McManamey⁷⁵, the method of calculating the values of the interfacial mass transfer coefficients suffers from inherent errors, since the calculation of mass transfer coefficients, in the absence of chemical reaction, is by means of empirical approximations. Another method of studying interfacial mass transfer is to use the variation of mass transfer rate with stirrer speed. The correlations of Lewis^{65,66}

and McManamey⁹⁴ give:-

$$K' = aS^{1.65} \text{ and } K' = aS^{0.9}$$

79.

respectively for mass transfer in the absence of chemical reaction. Experimental results, to be reported later in this thesis, for the transfer of 8-hydroxyquinoline, give

$$K' = a + bS$$

79a.

where K' is the mass transfer coefficient, S is the stirrer speed, equal for both stirrers, and a and b are constants. Assuming that the rate of chemical reaction is independent of stirrer speed, substituting 79 in 75 gives:-

$$1/K = 1/(a + bS) + 1/K_G$$

80.

If a is small compared with bS , equation 80 approximates to

$$1/K = 1/aS + 1/K_G$$

81.

and a reciprocal plot of mass transfer coefficient K against stirrer speed S will have a linear slope of $1/b$ and an intercept at $S = \infty$ of $1/K_G$. Providing the interfacial resistance is at least 50% of the total resistance, in the middle of the range of stirrer speeds studied, this analysis should provide values of K_G of the same order of accuracy as the measured values of K . This method of analysis will be used later in this thesis to determine the interfacial mass transfer coefficients for the transfer of metal ions to and from solutions of organic extractants in paraffin diluent.

2. EXPERIMENTAL METHODS AND TECHNIQUES

INTRODUCTION

The principal objective of the research described in this thesis was to study abnormally slow metal transfer processes, in which it was expected that mass transfer to and from the interface is not wholly rate determining under normal conditions of agitation. In Section 2, a résumé of the available methods of measuring mass transfer rates is given, and the method chosen is discussed in terms of the following conditions:-

- (a) Interfacial area to be determinable.
- (b) The two liquid phases to be agitated.
- (c) The hydrodynamic conditions to be reproducible, and the factors controlling them specified.
- (d) Facilities for control and analysis of the solutions to be available.

After a description of the analytical and experimental techniques used, the experimental work designed to characterise the apparatus will be described. Next the experimental survey of the kinetics of various metal extraction systems is discussed together with the choice of systems for more intensive study. Also, included here is a description of the measurement of factors necessary for interpretation of the kinetic measurements, viz. equilibrium measurements and determinations of diffusion coefficients, interfacial tensions and viscosities.

2.1 METHODS OF KINETIC MEASUREMENT

2.1.1 Choice of Method

In normal practice, solvent extraction is achieved by vigorous agitation leading to dispersion of one phase in the other. The resulting interfacial area is related to the distribution of drop size which is dependent on the agitation, vessel design and extraction system. Attempts have been made by Chester⁷⁸, Vermeulen⁷⁹⁻⁸⁰ and Rodgers⁸¹⁻⁸² to determine the interfacial area, but they found that the accuracy of their measurements was of a low order. For this reason the simple mixer cannot be used to obtain meaningful kinetic results. Other methods have, however, been devised in which the interface is closely defined. These methods can be divided into three

categories:-

- (a) Experiments in which the two phases are maintained static while in contact, and transfer is entirely by molecular diffusion. One disadvantage of the method is that the analytical techniques are limited to measuring the concentration profile by diffraction, refractive index⁸³, spectrophotometric or radio-isotope methods⁸⁴. Most of the published results have been obtained by one of the last two techniques.

One advantage of the unstirred system is that an exact mathematical treatment is possible, both with and without an interfacial resistance. However, in practice, the high bulk resistance to mass transfer of unstirred phases, together with the limited accuracy of measurement of concentration profiles, prevents the accurate determination of small interfacial resistances. Davies and Wiggill⁶⁷ used this method, and obtained results in close agreement with theory, except in those systems where spontaneous interfacial turbulence occurred. They found that the presence of surface active agents reduced the interfacial turbulence but, with the exception of sorbiton tetrastearate, did not produce any interfacial resistance.

- (b) The second method or technique which has been used extensively, particularly for the study of the effect of surface active agents on the rate of transfer, is the transfer to and from liquid drops. Initially this method appeared attractive, but thorough investigation showed that interfacial turbulence and internal circulation limit its usefulness. It has been found, however, that surface active agents eliminate both these phenomena almost entirely. Garner and Skelland⁸⁸⁻⁹² analysed the system mathematically treating the problem for its two extreme conditions; (a) when the drop is considered to be a solid body, and (b) when there is turbulent flow inside the drop with continual surface renewal. Equations based on these models are as follows:-

$$(a) \quad [Sh] = 0.8[Re]^{\frac{1}{2}}[Sc]^{-1/3} \quad 82.$$

$$(b) \quad [Sh] = 2/\pi[Re]^{\frac{1}{2}}[Sc]^{\frac{1}{2}} \quad 83.$$

where Sh is the Sherwood group defined as $[Sh] = kd/D$, where \underline{d} is the diameter of the drop, D is the diffusion coefficient and K is the mass transfer coefficient for the drop. Experiments carried out by Garner et al⁸⁸⁻⁹² gave results which fitted the following experimental correlation:-

$$[Sh] = -126 + 1.8 [Re]^{1/2} [Sc]^{-0.42}$$

84.

which shows that the conditions pertaining in their experiments were intermediate between the two extremes studied theoretically.

- (c) The final system for the measurement of mass transfer coefficients is that using a stirred cell with a static interface. The principle behind this method is that, as the distance over which mass transfer occurs is much smaller than in the static system, the bulk phase resistance is much smaller. However, except in the case of systems with high interfacial resistances, it is not found possible in practice to obtain a negligible bulk phase resistance and the rate is at least partly determined by transfer across the region of laminar flow near the interface.

Many attempts have been made to obtain a correlation between the rate of transfer of a simple solute, with negligible interfacial resistance, and the hydrodynamic variables. Lewis^{65,66} conducted a large number of experiments on a number of simple solute systems, over a wide variation of Reynolds and Schmidt numbers, and obtained the following correlation:-

$$k_{\alpha} = \sqrt{\alpha} [1.13 \times 10^{-7} (Re_{\alpha} + Re_{\beta} \gamma_{\beta} / \eta_{\alpha})^{1.65} + 0.0166]$$

85.

He found that certain of the systems he studied gave transfer rates higher than those predicted and that in these systems spontaneous interfacial turbulence was evident. Lewis found no evidence of any correlation between mass transfer coefficient and the Schmidt group. He considered that this was because the rate of transfer was controlled entirely by eddy diffusion and, to support his argument, used the fact that the relative direction of rotation of the two stirrers had no effect on the rate of transfer. Sherwood⁹³, however, felt that, even if the cell was stirred vigorously, to maintain a static interface a stagnant layer, if only a thin one, must be present and that the rate of transfer would be proportional to the Schmidt group to a power between 0 and -1: if one accepts Dankwerts theory of surface

renewal then the power will be -0.5 . In another paper Searle and Gordon²⁸ found that a power of -0.5 gave a close approximation to experimental results.

McManamey⁹⁴ has taken Lewis' results and re-correlated them with the Schmidt and Reynolds groups obtaining the following equation:-

$$k_{\alpha} = 6.4 \times 10^{-4} \gamma_{\alpha} [Sc_{\alpha}]^{-0.3} [Re_{\alpha}]^{0.9} (1 + Re_{\beta}^h / Re_{\alpha}^h) \quad 86.$$

Using a cell similar to that of Lewis, except for a different arrangement of the baffles, McManamey⁹⁴ obtained the following correlation for his own experimental results:-

$$k_{\alpha} = a \gamma_{\alpha} [Sc_{\alpha}]^{-0.37} [Re_{\alpha}]^{0.9} (1 + Re_{\beta}^h / Re_{\alpha}^h) \quad 87.$$

where a is 1.70×10^{-3} and 1.43×10^{-3} respectively for brass and glass stirrer units.

An attempt has been made by Olander⁹⁵ to analyse the flow near the interface in cells of this type using the Navier-Stokes equations. Having derived equations for the radial and axial velocities he then solved Fick's second law of diffusion to obtain an equation for the concentration gradient at the interface and hence obtained an equation for the mass transfer coefficient. His main conclusions were:

- (i) Mass transfer is impossible across the area of the interface directly under the stirrer paddle (known as the core region), since the concentration gradient here is zero. This result is difficult to accept and there is no experimental justification for it.
- (ii) The mass transfer coefficient in the region between the core and the edge of the cell (known as the annulus region) is given by the following relationship:-

$$[k_{\alpha} = B \gamma_{\alpha} (2\pi N_{\alpha} / \gamma_{\alpha})^{\frac{1}{2}} (Sc)^{-2/3}] \quad 88.$$

where B is a constant.

Although Olander's analysis has not been supported by experimental data, it does illustrate two points:

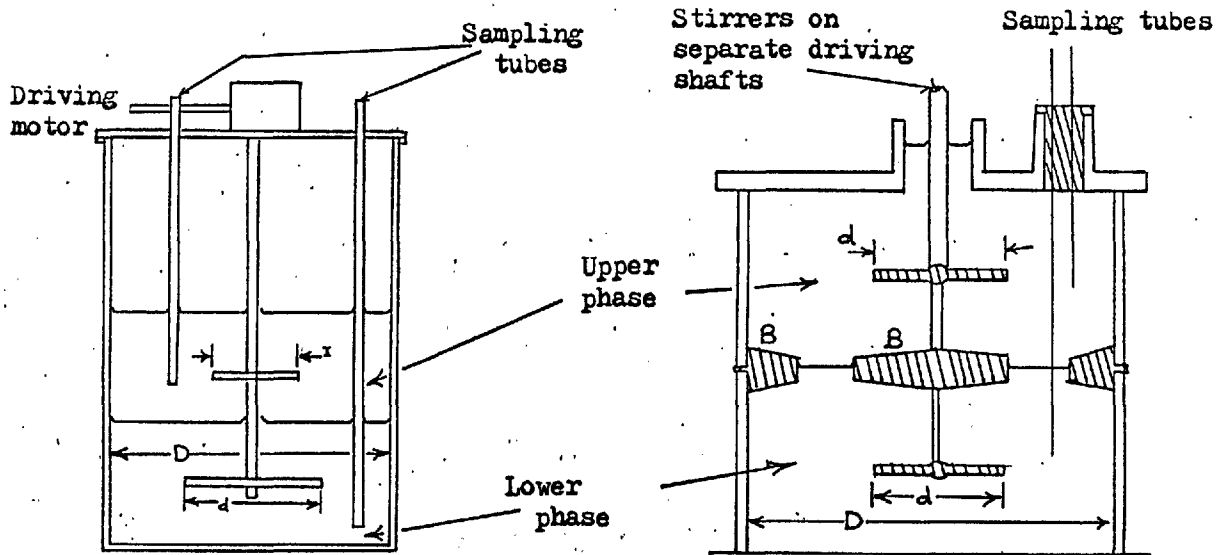
- (i) Even when mass transfer is controlled by molecular diffusion it may be possible for the mass transfer coefficient to be proportional to the Schmidt group to a power of less than one.

- (ii) Unless the stirrers are close to the interface, it is unlikely that the relative direction of the two stirrers is of any importance, because, with either 'co' or 'contra' rotating stirrers, the fluid tangential velocity, in the region of the interface, is small and the Navier-Stokes equations are reduced to two dimensional equations. Diagrams of typical cells of this type, used by various workers, are shown in Figure 1.

2.1.1(a) In addition to the three established methods of studying mass transfer already considered, there are also four novel methods worth mentioning.

- (i) Chester ⁷⁷ has described a method for determining concentration profiles across a steady state diffusion system. He used an aqueous phase kept in a saturated condition by a crystal of uranyl nitrate and studied the transfer of this species into a slow moving solution of T.B.P. in paraffin, the concentration of T.B.P. being high. He maintained that the method was extremely sensitive. The chief criticism of this method is that it cannot be used to study the influence of concentration in the aqueous phase.
- (ii) Martin ⁹⁶ has described a method by which a thin film of an organic phase, carried on the rim of a thin Teflon disc, is squeezed past an aqueous solution contained in a slit at the end of a Teflon tube, the organic phase being removed from the disc, after passing the slit, by a scraper. He maintained that, because the contact time was short, and agitation, due to the squeezing, high, no bulk concentration gradients were set up and the method would measure small interfacial resistances. As yet very few experimental results have been published using this method and the small volumes involved give rise to analytical difficulties.

FIG. I



$I=6.7\text{cm.}$ $d=10.2\text{cm.}$

$D=15.2\text{cm.}$

Phase volumes=1 litre.

Gordon & Sherwood (ref27).

B Baffle

$d=3.2\text{cm.}$

$D=10\text{cm.}$

Phase volumes=300ml.

Lewis(ref65).

COMPARISON OF STIRRED TRANSFER CELLS (static interface type)

Supporting rods for stirrer unit.

Driving pulleys.

Lower phase sampling assembly.

Upper phase sampling assembly.

$d=4\text{cm.}$

$D=8\text{cm.}$

Phase volumes=400ml.

McManamey (ref94).

- (iii) Vignes ⁹⁷ has developed a method by which unstirred bulk phases can be brought into interfacial contact and separated again, with a high phase recovery, for precisely defined contact times. The two phases are contained in two cylinders, which can be rotated to bring the phases into contact. They are subsequently separated by placing a thin sheet of Teflon between the two cylindrical blocks. Although this method provides a means of measuring the total transfer into an unstirred bulk over an accurately known period of time, it still has the inherent difficulty of high bulk phase resistances.
- (iv) Quinn and Jeanin ⁹⁸ measured the rate of transfer of iso-butanol, saturated with water, into a laminar jet of water. Contact time was varied by means of the jet length in the range 0.5 to 5 cm, this being the range over which stable jets were formed. They maintained that a small interfacial resistance existed in this system, which Lewis could not have detected using his stirred bulk phase static interface apparatus, since the sensitivity of their method was an order of magnitude higher than that of Lewis' method. It is significant that results obtained by this method were highly reproducible and not subject to any marked deviations. Results reported so far seem to indicate that surface active agents have no effect on rates of transfer measured by this method. This is in accord with the theory that the action of surface active agents is to modify the hydrodynamics of a system, since it is inconceivable that there could be any marked change in the hydrodynamic characteristics of a jet, as formed in these experiments. With regard to the conditions set out on page 32, it was decided to use a stirred bulk static interface type of system for the experimental work described in this thesis. This is because, of the three basic systems already described, it appears to be the most reproducible, subject to the lowest bulk phase resistance, while allowing facilities for control and analysis of the solutions available. Although many of the more novel methods appear to show promise of giving good results for measurements of mass transfer rates. The amount of published data on them is however scanty and it was decided to use a better established technique since the prime purpose of the work was to study certain extraction systems rather than the hydrodynamics of a new technique.

2.1.2 Description of the cell used

The final cell design used in the experimental work is shown in Figure II. In some of the earliest work a slightly different design was used so that the interfacial area could be varied. However, when results from the kinetic studies of the 8-hydroxyquinoline system showed that the rate of transfer per unit area was independent of the position of this area across the cell, this earlier cell was discarded, as it was more difficult to work with.

Stirrer discs were used in preference to stirrer bars as it was noted that stirrer bars produced a wave at the interface which unnecessarily complicated the hydrodynamic conditions. The discs were placed at equal distances on either side of the interface, were contra-rotated in all but one experiment and always rotated at the same speed as each other.

The overall dimensions of the cell were as follows:-

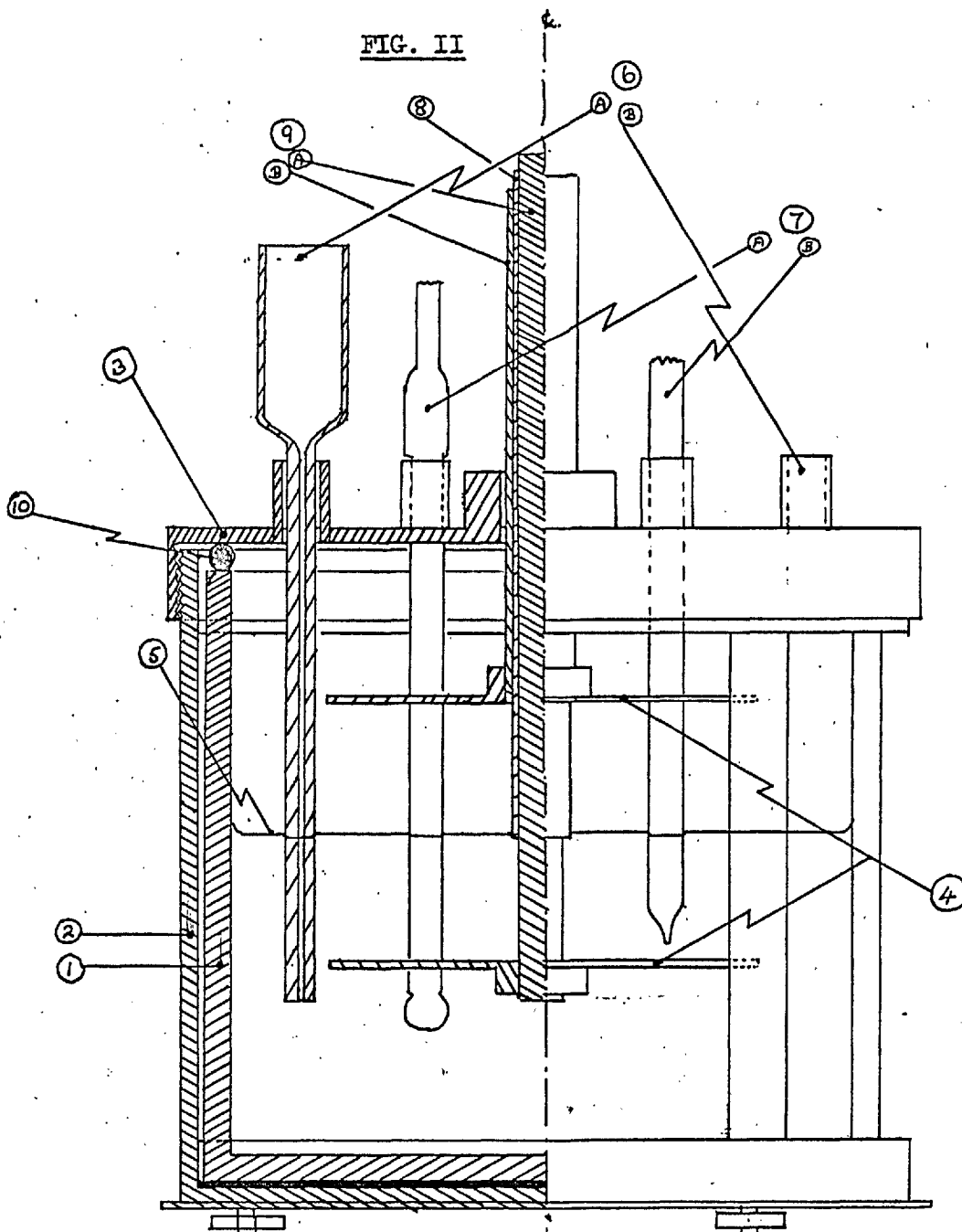
Cell height	=	8.50 cm.
Internal diameter	=	8.95 cm.
Phase Volume	=	260 cm ³ per phase
Stirrer disc diameter	=	6.3 cm.
" " thickness	=	0.15 cm.
Distance between disc and interface	=	1.9 cm.
Interfacial area	=	62.8 cm ²

The earlier cell had upper and lower phase volumes of 267 and 237 cm³ respectively and the interface was formed in the annulus between a flat ring attached to the main cylinder and a disc attached to a stationary central shaft.

Variations of interfacial area were obtained by removing the ring or disc or both. The various interfacial areas used were as follows:-

<u>External radius of the annulus</u>	<u>Internal radius of the annulus</u>	<u>Interfacial Area</u>
2.55 cm.	1.92 cm.	8.9 cm ²
2.55 "	0.33 "	20.1 "
4.48 "	1.92 "	51.3 "
4.48 "	0.33 "	62.6 "

FIG. II



EXPERIMENTAL TRANSFER CELL. (Half Sectioned)

- KEY**
- | | |
|--------------------------------|-------------------------|
| 1. Glass Cell. | 7. pH Probes. |
| 2. Cell Holder (Brass). | A. Glass Electrode. |
| 3. Cell Lid (Stainless Steel). | B. Reference Electrode. |
| 4. Stirring Discs. | 8. Fixed Shaft. |
| 5. Liquid Interface. | 9. Rotating Shafts. |
| 6. Sample Ports. | A. Lower Disc. |
| A. Aqueous Phase. | B. Upper Disc. |
| B. Organic Phase. | 10. 'O' Ring (Teflon). |

(The thermometer port has been omitted for clarity).

The stirrer discs were driven from a common motor by spring-belt drives, a single twist being put in one of the spring belts to obtain contra-rotation. In the earlier work the motor used was of the synchronous type fitted with a worm gear reducer. This type of motor ensured constant stirrer speed throughout an experiment, change of stirrer speed being effected by changing the worm gear ratio and the size of the pulleys on the gear shaft. For much of the experimental work quick changes of speed had to be made. For this the synchronous motor was replaced by a D.C. motor, with both its field and armature windings fed from stabilised voltage supplies. In this way it was possible to change quickly from one to another of five reproducible stirring speeds. The field winding of the motor was fed from a transistor and Zener diode fixed voltage supply of 9.1 volts and the armature winding was fed from a variable valve-stabilised voltage supply with a selection of fixed outputs between 40 and 160 volts. Using an appropriate worm reduction gear, five stirrer speeds between 25 and 120 r.p.m. were obtained. Within the period of one run, these speeds varied by $\pm 1\%$, from one run to another, the speed for a particular power supply setting varied by $\pm 5\%$. The circuits for these power supplies are shown in Figure III.

The pH of the aqueous phase, in some experiments, was monitored continuously using an E.I.L. glass electrode and a Pye calomel electrode. These were inserted through the top of the cell and the upper organic phase with the sensitive ends in the aqueous phase; the pH was measured on a direct reading Pye pH meter. Sampling of both phases was by means of pipettes. In the case of the aqueous phase the sample was drawn up through a capillary tube into a sample tube before taking the sample.

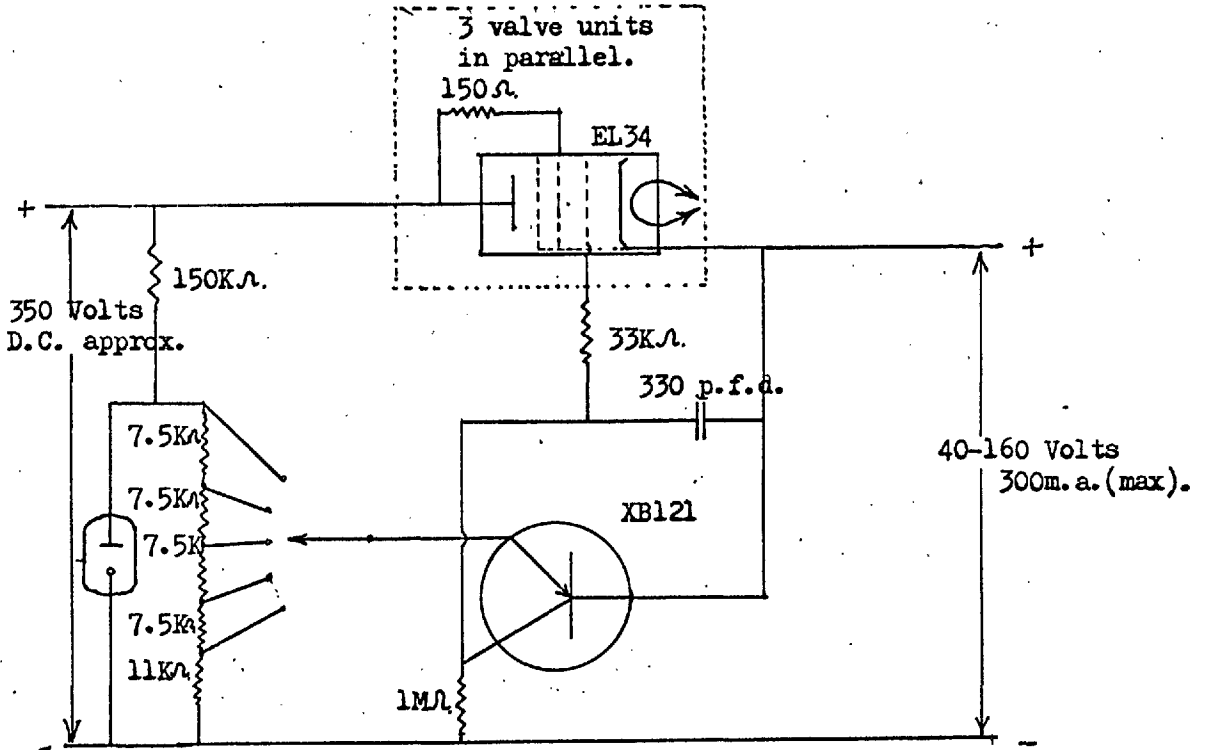
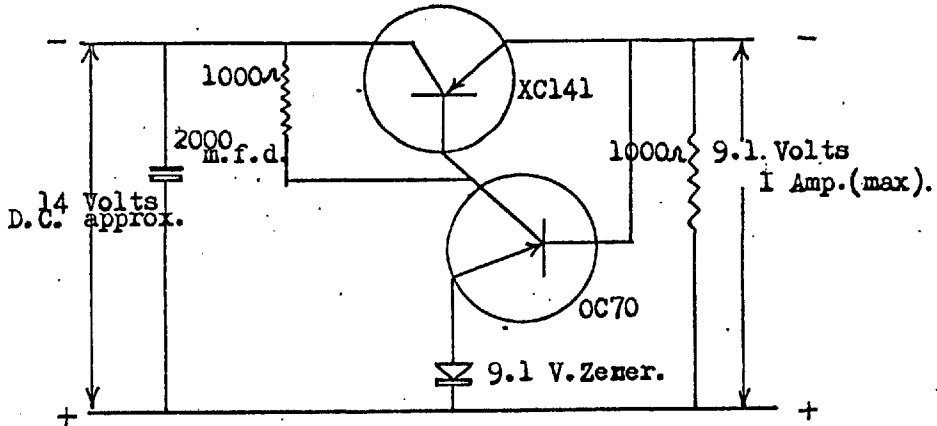
2.2 Materials Used

2.2.1 Inorganic materials

All solutions used for kinetic measurements and analytical work were prepared from Analytical Reagent grade except where this was unobtainable. In such circumstances the fact will be stated when reference is made to the material.

FIG. III

9.1 VOLTS CONSTANT FIELD SUPPLY.



ARMATURE SUPPLY, 40-160 VOLTS IN FIVE STEPS.

2.2.2 Organic materials

Commercial grade paraffin was used, which was purified first by passing it over two charcoal columns and finally by passing it over two activated alumina columns. A very small quantity of waxoline O.S. red dye was added to the paraffin, before any purification, to ensure that the charcoal was replenished when break through occurred, the alumina being changed when the small band of yellow discoloration at the top of the second column started to progress down. The following organic extraction reagents were used :-

- (i) tri-iso-octylamine
- (ii) naphthenic acid.
- (iii) tri-butyl phosphate
- (iv) di-2-ethylhexyl-phosphoric acid

The first reagent was obtained from B. Newton Maine Ltd., the second from the Shell Chemical Company Ltd., and the last two from Albright & Wilson Ltd. The first three compounds were used as obtained, without further purification, however, the last compound, which was used for most of the kinetic studies, was purified further in the following manner. Firstly, it was stirred with 5 N hydrochloric acid at 60° C for twelve hours. After cooling, the hydrochloric acid was separated and the reagent was washed thoroughly with water in a separating flask. It was then diluted with paraffin to 2 M, shaken with 3 equal volumes of ethylene glycol and thoroughly washed again. It was next shaken with an excess of 2 N solution of sodium carbonate, the bottom, (aqueous), phase of the three run off, and that remaining washed again with a small quantity 2 N sodium carbonate, the bottom phase again being run off. The two remaining phases were then carefully acidified with a slight excess of 2 N hydrochloric acid to reform the acid, the aqueous phase was run off, and the organic material given a final wash with several volumes of distilled water. The organic solution was then assayed for di-2-ethylhexyl-phosphoric acid by titration with sodium hydroxide using a pH meter. If any of the mono acid remained as an impurity two points of inflexion in the pH versus volume of alkali curve occurred. Of the three reagents used without purification only thenaphthenic acid was a crude product; both the other two reagents were quoted as being 98% pure by the manufacturers. In some of the kinetic experiments

2-ethylhexyl alcohol was used as an additive; this was obtained as a reagent grade product.

2.2.3 Cleaning of equipment

In view of the significant effects of surface active agents on mass transfer rates, no detergents were used for cleaning purposes. Glassware was cleaned with chromic-sulphuric acid and water and all equipment coming into contact with organic solutions was cleaned with acetone and dried with compressed air. The water used throughout the experimental work was once distilled.

2.2.4 Preparation of metal organic solutions

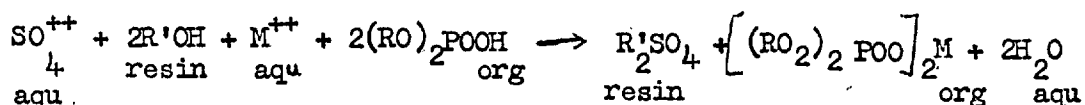
Many of the experiments carried out were for the purpose of studying the rate of stripping of metals from di-2-ethylhexyl-phosphoric acid in paraffin by dilute solutions of sulphuric acid. The simplest method of preparing these organo-metallic solutions is to extract the metal ions from solutions buffered at a pH of approximately 6 with acetic acid and ammonium acetate. Using this method the acid generated during extraction is neutralised. However, under these conditions, significant quantities of ammonium organo-phosphate are extracted into the organic phase and it is suspected that this affects the transfer rate in two ways:-

- (a) By causing a small amount of emulsification during the stripping reaction.
- (b) By competition for stripping between the metal ion desired and the cation associated with the neutralising base.

A new method of preparation was devised to produce solutions of organo-metallic phosphates containing only free acid and the metal phosphate required.

A strong base ion exchange resin in the hydroxyl form is ideal for the purpose of neutralisation, since the cations are part of the resin structure and cannot be extracted: the resin used was De-Acidite-F.F. in the bead form.

The overall equation for this reaction may be written as :-



Sufficient resin was used to give 40% loading of the available sites when complete neutralisation occurred, thus ensuring a final pH of approximately 6. The technique used was to add the resin, in the hydroxyl form, to a mixture of the two phases and agitate the three phases gently for one hour. The resin was removed by filtering on a coarse sintered glass filter and the organic phase was then decanted off. Last traces of the aqueous phase were removed by filtration through a fine sintered glass filter. In this way an organo-metallic solution in paraffin was obtained which contained only the metal complex and excess dialkyl phosphoric acid. One disadvantage of this method is that small traces of surface active material, originating from the resin, may contaminate the organic phase.

2.3. Experimental Techniques

2.3.1 Kinetic Measurements

The cell, set up as shown in Figure II, was immersed in a circular glass tank, fitted with a thermostat capable of maintaining the temperature constant to within $\pm 0.05^\circ\text{C}$. The lower (aqueous) phase was put in the cell and a sample of the upper (organic) phase, put in a graduated flask, was put in the thermostatic bath, and allowed to come to thermal equilibrium. During the warming up period the stirrer motor was run to allow it to come to constant speed.

When thermal equilibrium had been obtained, the stirrer motor was temporarily stopped and the upper phase added to the cell in such a manner as to prevent mixing of the two phases. The motor was then restarted and samples taken from one of the phases at suitable time intervals. As unbuffered aqueous solutions were used in certain experiments, for stripping metals, additions of sulphuric acid were made, by means of a hypodermic syringe, to maintain a constant pH.

2.3.2 Viscosity Measurements of Organic Solutions

The viscosities of the organic solutions used were measured and the results were applied as follows:-

- (a) For the calculation of diffusion coefficients, using Einstein's equation.
- (b) For calculation of the Schmidt and Reynolds numbers which were used in calculating individual film coefficients.
- (c) To check for the presence or absence of any abnormally high viscosities, which often indicate that polymerisation is taking place.

The apparatus used for the viscosity measurements was an Ostwald viscometer, calibrated using aqueous glycerol solutions. The measurements were made at $20^{\circ}\text{C} \pm 1^{\circ}$ and were carried out in triplicate.

2.3.3 Interfacial Tension Measurements

The interfacial tension between solutions of metal organo-phosphate and solutions of dilute sulphuric acid was determined by measuring the volume of drops of one phase formed slowly in the other phase. Drops of the aqueous solution were formed at the end of a glass tube dipped in the organic solution. The aqueous solution was delivered by means of a hypodermic syringe and the end of the tube on which the drops were formed was ground smooth at right angles, using a grinding wheel. During formation of the drops, the aqueous solution was added at a fairly fast rate until just before the drop broke away from the end of the tube. The last stage of drop formation was carried out very slowly, each drop taking about 30 seconds. The volume measured was that between the break away of successive drops. For each interfacial measurement, three drop volumes were obtained and the average taken. From the drop volume the interfacial tension was determined using the following formula (Adam)⁹⁹:-

$$\gamma = VF (\rho_w - \rho_o)g/r$$

89.

where V is the volume of the drop, r is the external radius of the tube (as the drop formed on the external radius), $(\rho_w - \rho_o)$ is the difference in the densities of the two phases, γ is the

interfacial tension and F is introduced to account for the non-sphericity of the drop; values of this factor have been tabulated as a function of V/r^3 by Adam⁹⁹.

2.3.4 Diffusion Coefficient Measurements

The diffusion coefficients of simple metal salts in aqueous solution can be determined from the equivalent conductances of the individual ions, using the equation:-

$$D^{\circ} = 2.662 \times 10^{-7} \left[(Z_1 + Z_2)/Z_1 Z_2 \right] \left[\Lambda^{\circ}_1 \Lambda^{\circ}_2 / (\Lambda^{\circ}_1 + \Lambda^{\circ}_2) \right] \quad 90.$$

where Z_1 and Z_2 are the valencies and Λ°_1 and Λ°_2 are the equivalent conductances of the individual ions, at infinite dilution, and D° is the diffusion coefficient at infinite dilution. At low ionic strengths < 0.01 M there is little change in diffusion coefficient with ionic strength. For larger, complex molecules in aqueous or organic solutions, it is possible to obtain approximate values for the diffusion coefficients using Einstein's equation:-

$$D = (RT/3\eta) (\rho/6\pi^2 N^2 M)^{1/3} \quad 90a.$$

where R is the gas constant

T the absolute temperature

η is the viscosity of the solution

ρ is the density of the solution

N is Avogadro's number, and

M is the molecular weight of the diffusing species.

However, this equation is only an approximation, so it was decided to determine, experimentally, some diffusion coefficients for comparison. The basis of the method used was the diffusion of solute from a capillary. The technique employed was a modified version of that of Hills and Djordjevic¹⁰⁰ in which the solute diffused from the capillary--like pores of a number 4 sintered glass disc, 1.2 cm. in diameter and 0.62 cm. thick. The disc was saturated in a solution of known strength, the surplus being allowed to drain off, and suspended in a large volume of the solvent, 500 ml approximately. The disc was rotated slowly for a known length of time and then removed from the solvent. The solution remaining in the disc was removed and its concentration determined. If T is the thickness of the disc, x a distance measured from the centre of the disc and perpendicular to the face, t is the time of diffusion and \bar{C} the

average concentration of solute left in the disc after a time t , the boundary conditions for the diffusion are:-

$$C = C_0, -T/2 < x < T/2, \text{ when } t = 0$$

$$C = 0, -T/2 > x > T/2, \text{ for all values of } t$$

and \bar{C} is given by the equation:-

$$\bar{C} = (8 C_0 / \pi^2) \left(\sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[- \left[(2n+1) \pi^2 D' t / T^2 \right] \right] \right) \quad 91.$$

where D' is the apparent diffusion coefficient, related to the true diffusion coefficient D , by the equation:-

$$D' = D/L \quad 92.$$

where L is the labyrinth factor. The labyrinth factor is defined as the relative increase in the average path length, arising from the tortuous nature of the pores, and can be calculated from the equation:-

$$L = R P A K / T \quad 93.$$

where R is the electrical resistance between the faces of the disc soaked in a solution of specific conductivity K , A is the area of the face of the disc and P the porosity of the disc, i.e. the fraction of the disc occupied by voids.

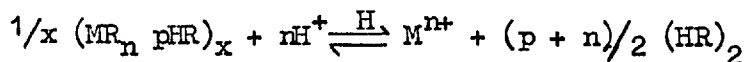
2.3.5 Equilibrium Constant Determinations

Equilibrium constants, for the three metal organo-phosphate systems studied kinetically, were required for two purposes:-

- (a) To calculate the distribution coefficient at varying levels of D.E.H.P. concentration and pH. The distribution coefficient is required in the calculation of mass transfer coefficients from the kinetic results (see page 88).
- (b) To elucidate the molecular formulae of the three metal complexes, for use in diffusion coefficient calculation by Einstein's formula (see page 47).

The reasons for the choice of the three metal organo-phosphate systems for detailed studies will be given later.

If the molecular formula of the metal complex is written as $(MR_n pHR)_x$ (where M is the metal species and R the organo-phosphate radical), then the overall equation for the exchange is



and the equilibrium condition is

$$1/H = [(MR_n pHR)_x]^{1/x} [H^+]^n \frac{A}{[M^{n+}]} [(HR)_2]^{(p+n)/2} \quad 94.$$

where A is an activity coefficient term.

Replacing the metal complex concentration by M_o and M^{n+} by M_a and expressing the concentration of D.E.H.P. in terms of the monomer gives:-

$$1/H = A [M_o]^{1/x} [H^+]^n [2]^{(p+n)/2} / [M_a] [HR]^{(p+n)/2} \quad 95.$$

If the distribution coefficient m is defined by $m = M_a/M_o$ and the total metal concentration by M_t

$$\left[\text{where } M_t = M_a + M_o \text{ for equal phase volumes} \right]$$

then equating the logarithm of each side gives the following equation:-

$$\left[(p+n)/2 \log 2 + \log A \right] - n pH + \log H = (p+n)/2 \log [HR] + \log m + \left[(x-1)/x \right] \log [M_t / (1+m)] \quad 96.$$

The values of ' m ' were determined experimentally using the following technique:- equal portions of aqueous phase, containing the metal ion, and organic phase were shaken together.

The metal ion concentration was 10^{-3} M or less and the D.E.H.P. concentration was 0.05 M or more. The aqueous solution was buffered with acetic acid and ammonium acetate for Ni^{++} and Co^{++} , and monochloroacetic acid and ammonium chloroacetate for Cu^{++} , the buffer strength being 0.1 M in all cases. After phase disengagement, assisted by centrifuging where necessary, the phases were sampled and analysed. By studying the variation of m with changes in M_t , D.E.H.P. concentration and pH, the values of x , n and p for each complex were determined.

2.4 Analytical Techniques

In this work four systems were studied in detail, and for these systems an accurate method of analysis was required. However, in addition to these systems, analyses of a less precise nature were needed for those systems which were surveyed but not studied in detail. These analyses mostly involved titration with ethylenediaminetetracetic acid (E.D.T.A.) and it is not necessary to go fully into all these analyses. The four systems studied in detail required precise determination of the following components:-

- (a) 8-hydroxyquinoline
- (b) Copper
- (c) Nickel
- (d) Cobalt

The techniques for these analyses were as follows:-

2.4.1 8-hydroxyquinoline

This substance was determined spectrophotometrically in paraffin at a wavelength of 3315 \AA . The technique was to take the sample, in paraffin, dilute to approximately 2×10^{-4} molar and measure its optical density against a paraffin blank, using 10 mm. cells in a Unicam S.P.500 spectrophotometer.

2.4.2 Copper

For the analyses of both copper and nickel it was necessary to obtain the sample in aqueous solution and all organic solutions were first stripped, by shaking with an excess of 0.1 M sulphuric acid. Copper was determined spectrophotometrically, using rubeanic acid as a colour developing reagent. The technique was to take a suitable quantity of the aqueous solution, add to it 1 cc. of a strong buffer solution of pH 4.5, 2 cc. 0.5% gum-acacia solution and 5 cc. of 0.01% rubeanic acid. This was diluted to 25 cc. and, after standing for half-an-hour, its optical density measured at $6,300 \text{ \AA}$ against a reagent blank.

2.4.3 Nickel

As with copper, nickel was analysed spectrophotometrically, using quinoxaline-2,3-dithiol as a colour developing agent. The technique was to take a suitable quantity of the nickel solution, add 10 cc. of 0.880 ammonia and exactly 3 cc. of an 0.02 M solution of the reagent in ammonia. This was diluted to 25 cc. and, after

standing for half-an-hour, its optical density was measured at 5,200 Å against a reagent blank. In view of the absorbancy of the reagent at this wavelength it is essential to use both, exactly the same concentration of reagent throughout and a concentration which is in sufficient excess such that the quantity used for complex formation is insignificant.

Calibration tables and graphs for the 8-hydroxyquinoline, copper and nickel analyses can be found in Appendix I.

2.4.4 Cobalt

Cobalt was analysed by means of the radio-isotope Co^{60} , which has a half-life of 5.25 years and emits gamma rays of 1.17 meV and 1.33 meV. The gamma emissions were counted in an I.D.L. scintillation counter, using a thallium-activated potassium iodide crystal.

Initially, a standard solution of cobalt was made up with a suitable quantity of tracer added and all other solutions were made by dilution of this standard. Using this technique, the analysis of any sample, aqueous or organic, was carried out by a comparison of the count rate of a standard quantity of the sample (3 c.c.) with the count rate of an equal quantity of a standard solution.

3. EXPERIMENTAL RESULTS

3.1 EQUILIBRIUM RESULTS

The equilibrium distributions of copper, nickel and cobalt between buffer solutions and solutions of D.E.H.P. in paraffin were studied as functions of the variables; metal concentration; pH, D.E.H.P. concentration and temperature. The effect of addition of 2-ethylhexyl alcohol (capryl alcohol) was also studied. The results of these experiments were as follows:-

TABLE I. Equilibrium distributions as a function of total metal concentration at 20°C with D.E.H.P. concentration 0.10 mole/litre.

(a) Copper - equilibrium pH 2.90.

Total Conc. M_t mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	m $= M_a/M_o$
4×10^{-3}	2.55×10^{-3}	1.40×10^{-3}	1.81
9×10^{-4}	5.85×10^{-4}	3.15×10^{-4}	1.85
3×10^{-4}	1.95×10^{-4}	1.10×10^{-4}	1.79
1×10^{-4}	0.65×10^{-4}	0.35×10^{-4}	1.85

(b) Nickel - equilibrium pH 3.75.

Total Conc. M_t mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	m $= M_a/M_o$
1×10^{-3}	6.15×10^{-4}	3.65×10^{-4}	1.68
3.5×10^{-4}	1.95×10^{-4}	1.30×10^{-4}	1.50
1.2×10^{-4}	7.00×10^{-5}	4.30×10^{-5}	1.63
3.5×10^{-5}	2.20×10^{-5}	1.30×10^{-5}	1.69

(c) Cobalt - equilibrium pH 3.55.

Total Conc. M_t mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	m $= M_a/M_o$
1×10^{-3}	5.10×10^{-4}	4.65×10^{-4}	1.10
4×10^{-4}	2.05×10^{-4}	1.90×10^{-4}	1.09
1×10^{-4}	5.20×10^{-5}	4.80×10^{-5}	1.08
6×10^{-5}	3.05×10^{-5}	2.90×10^{-5}	1.05
2×10^{-5}	1.00×10^{-5}	0.95×10^{-5}	1.05

TABLE II. Equilibrium distributions as a function of pH at 20°C with total metal concentration (M_t) 10^{-3} mole/litre and D.E.H.P. concentration 0.10 mole/litre.

(a) Copper

pH	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	$m =$ M_a/M_o	log m .
2.80	7.50×10^{-4}	2.50×10^{-4}	3.00	0.478
3.00	6.20×10^{-4}	3.85×10^{-4}	1.60	0.204
3.15	4.75×10^{-4}	5.20×10^{-4}	0.91	-0.041
3.25	3.65×10^{-4}	6.45×10^{-4}	0.568	-0.246
3.35	2.70×10^{-4}	7.05×10^{-4}	0.374	-0.427
3.45	2.00×10^{-4}	8.00×10^{-4}	0.250	-0.600

(b) Cobalt

pH	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	$m =$ M_a/M_o	log m .
3.25	8.20×10^{-4}	1.70×10^{-4}	4.82	0.683
3.30	7.90×10^{-4}	2.05×10^{-4}	3.84	0.585
3.55	5.20×10^{-4}	4.70×10^{-4}	1.10	0.042
3.70	4.05×10^{-4}	5.95×10^{-4}	0.678	-0.202
3.90	2.75×10^{-4}	7.25×10^{-4}	0.379	-0.421
4.10	1.50×10^{-4}	8.50×10^{-4}	0.174	-0.760
4.30	6.50×10^{-5}	9.40×10^{-4}	0.069	-1.160
4.40	3.80×10^{-5}	9.50×10^{-4}	0.040	-1.398

(c) Nickel

pH	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	$m =$ M_a/M_o	log m .
3.20	9.05×10^{-4}	6.80×10^{-5}	13.3	1.124
3.30	8.95×10^{-4}	1.25×10^{-4}	7.16	0.855
3.50	8.15×10^{-4}	1.85×10^{-4}	4.41	0.644
3.70	6.70×10^{-4}	3.30×10^{-4}	2.03	0.308
3.80	6.10×10^{-4}	4.15×10^{-4}	1.47	0.167
3.95	4.35×10^{-4}	5.35×10^{-4}	0.813	-0.090
4.15	2.40×10^{-4}	7.20×10^{-4}	0.333	-0.478
4.30	1.60×10^{-4}	7.90×10^{-4}	0.203	-0.692

TABLE III. Equilibrium distributions as a function of D.E.H.P. concentration at 20°C with total metal concentration (M_t) 10^{-3} mole/litre.

(a) Copper pH 3.00

D.E.H.P. Conc. mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	$m =$ M_a / M_o	log m.
0.4	4.80×10^{-5}	8.60×10^{-4}	0.056	-1.252
0.2	2.25×10^{-4}	7.25×10^{-4}	0.324	-0.490
0.1	6.20×10^{-4}	3.85×10^{-4}	1.60	0.204
0.05	9.20×10^{-4}	8.60×10^{-5}	10.7	1.029

(b) Cobalt pH 3.30

D.E.H.P. Conc. mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	$m =$ M_a / M_o	log m.
0.4	1.55×10^{-4}	8.45×10^{-4}	0.183	-0.738
0.2	4.70×10^{-4}	5.30×10^{-4}	0.886	-0.052
0.1	7.90×10^{-4}	2.00×10^{-4}	3.95	0.597
0.05	9.35×10^{-4}	5.60×10^{-5}	16.7	1.223

(c) Nickel pH 3.75

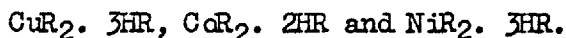
D.E.H.P. Conc. mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	$m =$ M_a / M_o	log m.
0.4	7.10×10^{-5}	9.40×10^{-4}	0.076	-1.118
0.2	3.50×10^{-4}	6.75×10^{-4}	0.515	-0.288
0.1	6.15×10^{-4}	3.65×10^{-4}	1.69	0.230
0.05	11.75×10^{-4}	9.50×10^{-5}	12.4	1.094

From Table I it can be seen that, for all three metals, the distribution coefficient, m , is independent of the value of M_t . Hence the value of x , in equation 96 (page 49), is 1 and equation 96 reduces to

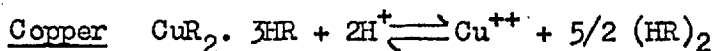
$$\left[(p + n)/2 \log 2 + \log A \right] - n\text{pH} + \log M = \log m + (p + n)/2 \log [\text{MR}] \quad 97.$$

From the results in Table II, graphs of $\log m$ against pH have been plotted in Fig. IV. The slopes $\left\{ \frac{\delta \log m}{\delta \text{pH}} \right\}_{(\text{HR})}$ have been found to be -1.78, -1.66 and -1.66 respectively for nickel, copper and cobalt. Differentiation of equation 97 shows that the slopes of these graphs are equal to $-n$ and hence the value of n , for all three metals, to the nearest integer, is 2.

From the results in Table III, graphs of $\log m$ against $\log [\text{HR}]$ have been plotted in Fig. V. The slopes $\left\{ \frac{\delta \log m}{\delta \log [\text{HR}]} \right\}_{\text{pH}}$ have been found to be -2.50, -2.15 and -2.50 respectively for copper, cobalt and nickel. Differentiation of equation 97 shows that these slopes are equal to $(p + n)/2$. Taking n equal to 2 gives values of p of 3, 2 and 3 respectively to the nearest integer and hence metal complexes with the following formulae:-



The equilibrium equations for these three complexes are:-

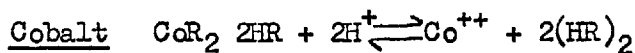


$$H = \frac{[\text{Cu}^{++}] [(\text{HR})_2]^{5/2} \gamma_{\text{Cu}^{++}} \gamma_{(\text{HR})_2}^{5/2}}{[\text{CuR}_2 \cdot 3\text{HR}] [\text{H}^+]^2 \gamma_{\text{CuR}}} \quad 98.$$

The activity coefficient of copper in an aqueous solution depends on the ionic-strength I , where $I = 1/2 \sum C_i Z_i^2$. In the buffer solutions used in the distribution measurements I was approximately 10^{-1} , from which it can be determined that $\gamma_{\text{Cu}^{++}} \approx 0.32$ and hence

$$H^4 = H \gamma_{\text{CuR}} / \gamma_{(\text{HR})_2}^{5/2} = 3.2 \times 10^2 \quad 98a.$$

Similar calculations for cobalt and nickel lead to:-



$$\text{hence} \quad H = \frac{[\text{Co}^{++}] [(\text{HR})_2]^2 \gamma_{\text{Co}^{++}} \gamma_{(\text{HR})_2}^2}{[\text{CoR}_2 \cdot 2\text{HR}] [\text{H}^+]^2 \gamma_{\text{CoR}}} \quad 99.$$

FIG. IV

Graphs of $\text{pH} \nu \log m$ for the equilibrium distribution studies.

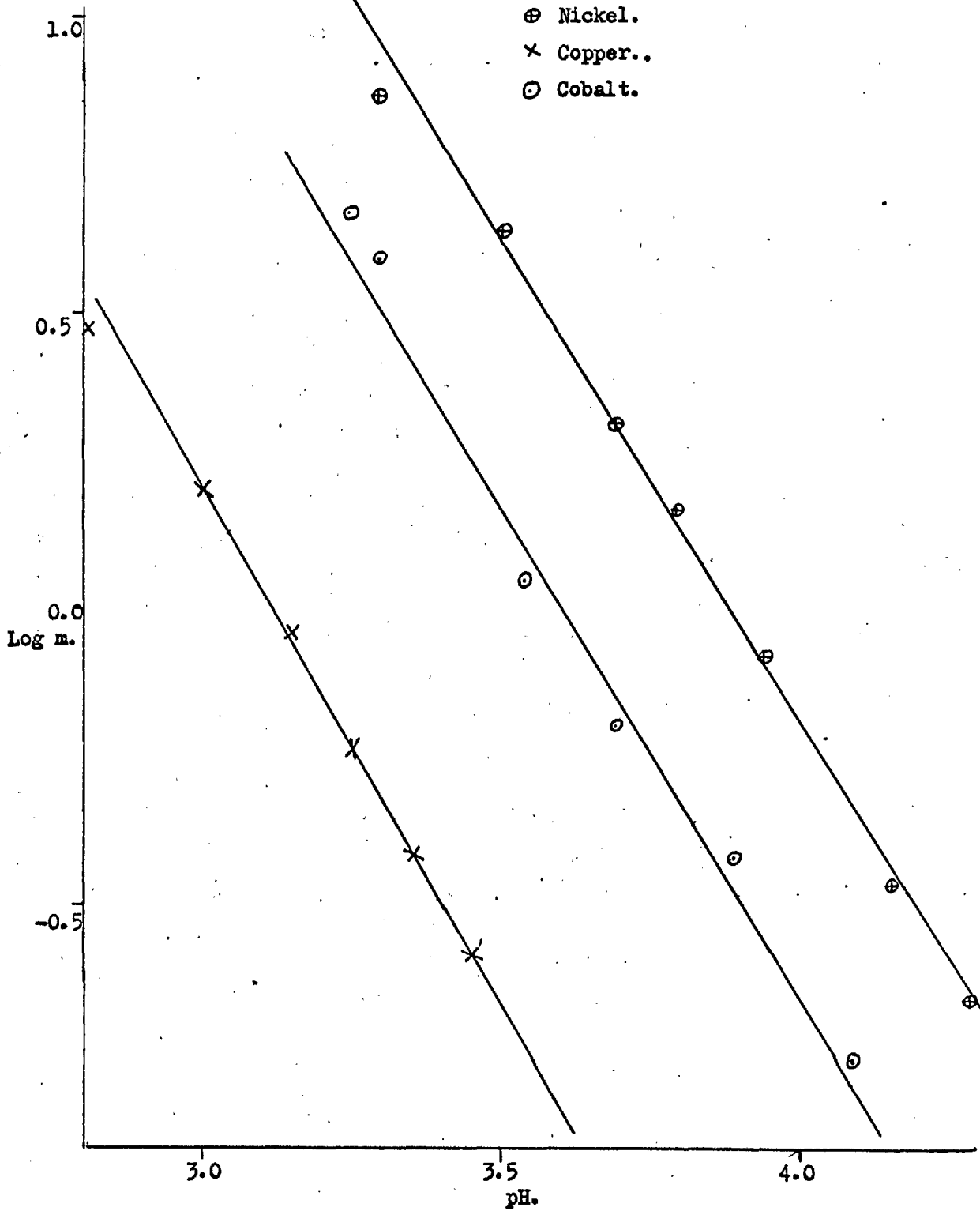
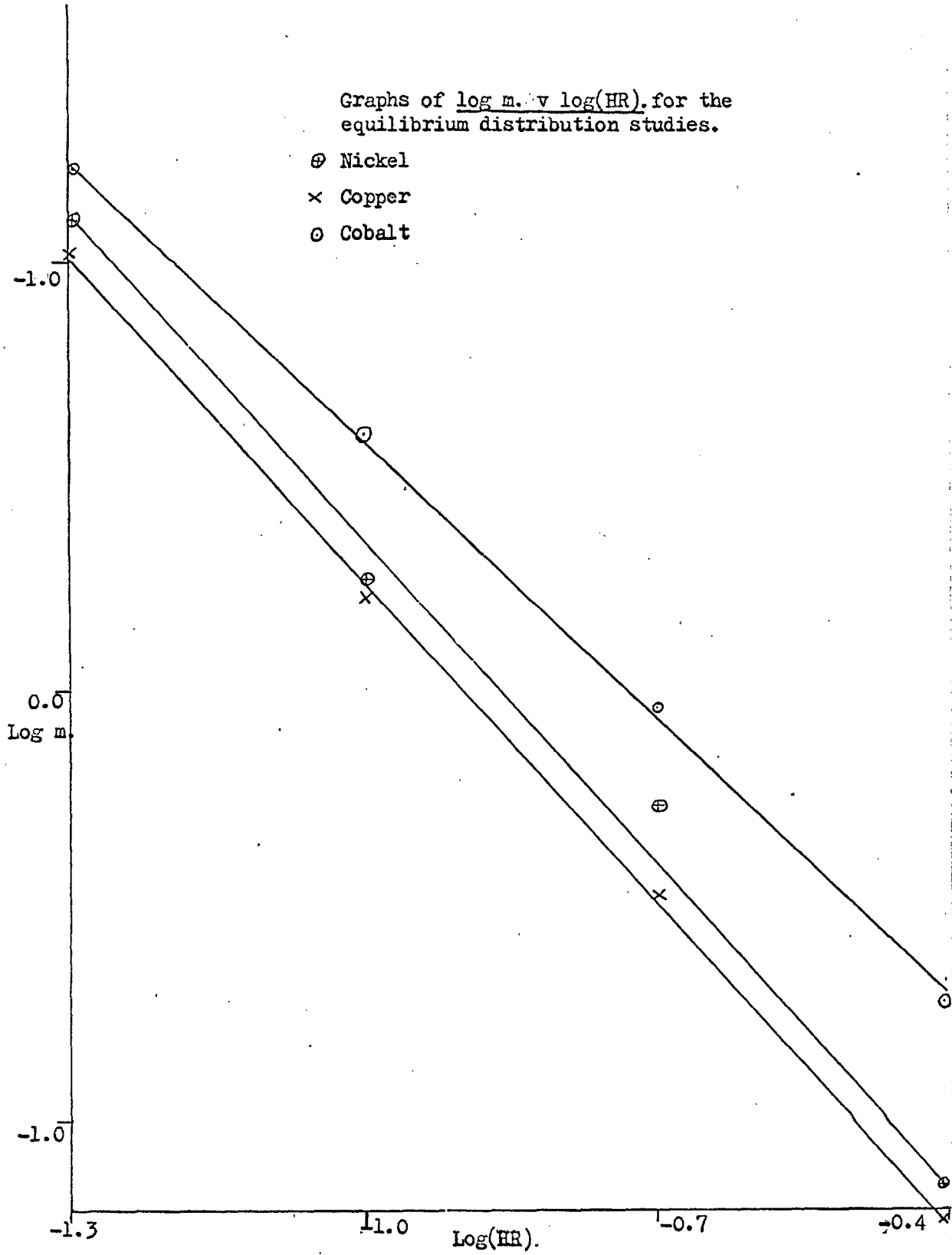
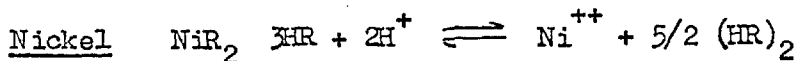


FIG. V



$$\text{and } H' = H \frac{\gamma_{\text{CoR}}}{\gamma_{(\text{HR})_2}^2} = 1.10 \times 10^4 \quad 99a$$



$$\text{hence } H = \frac{[\text{Ni}^{++}] [(\text{HR})_2]^{5/2}}{[\text{NiR}_2] [\text{HR}]^3 [\text{H}^+]^2} \frac{\gamma_{\text{Ni}^{++}} \gamma_{(\text{HR})_2}^{5/2}}{\gamma_{\text{NiR}}} \quad 100$$

$$H' = H \frac{\gamma_{\text{NiR}}}{\gamma_{(\text{HR})_2}^{5/2}} = 1.26 \times 10^4 \quad 100a$$

Values of m , to be used later for analysis of kinetic data, can be obtained from the equations

$$(a) \text{ Copper } \log m = 2.50 - 1.75 \text{ pH} - \log \gamma_{\text{Cu}^{++}} - 2.50 \log (\text{HR}) \quad 101a.$$

$$(b) \text{ Cobalt } \log m = 3.36 - 1.66 \text{ pH} - \log \gamma_{\text{Cu}^{++}} - 2.15 \log (\text{HR}) \quad 101b.$$

$$(c) \text{ Nickel } \log m = 3.53 - 1.65 \text{ pH} - \log \gamma_{\text{Ni}^{++}} - 2.50 \log (\text{HR}) \quad 101c.$$

In these equations actual experimental values of p and n (rather than nearest whole numbers) have been used.

3.1.1 The Effect of Temperature

From the values of H' obtained at various temperatures, the free energy of the reaction can be found using the equation

$$\Delta G^\circ = -RT_K \text{Ln} H = -RT_K \text{Ln} H' \quad 102$$

(assuming $\text{Ln} \left[\frac{\gamma_{\text{NiR}}}{\gamma_{(\text{HR})_2}^{5/2}} \right]$ is small)

Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, where ΔH° and ΔS° are the standard changes in heat content and entropy of the reaction respectively, by studying the variation of H' with temperature, the value of ΔH° can be calculated from the equation

$$\frac{\partial \text{Ln} H'}{\partial (1/T_K)} = -\Delta H^\circ / R \quad 103$$

This assumes that ΔH° and ΔS° are independent of T over the range considered. The experimental conditions used and results obtained in studying the effect of temperature on the equilibrium distributions are as follows :-

TABLE IV. Equilibrium distributions as a function of temperature with total metal concentration (M_t) = 10^{-3} M and D.E.H.P. concentration 0.1 M.

(a) Copper - equilibrium pH [at experimental temperature] = 3.10

Temperature °C.	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	H'	$\ln H'$
20	4.65×10^{-4}	4.55×10^{-4}	2.92×10^2	5.68
30	4.10×10^{-4}	5.00×10^{-4}	2.35×10^2	5.45
40	3.90×10^{-4}	5.20×10^{-4}	2.15×10^2	5.36
50	3.25×10^{-4}	5.90×10^{-4}	1.55×10^2	5.04

(b) Cobalt - equilibrium pH = 3.40

Temperature °C	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	H'	$\ln H'$
20	7.10×10^{-4}	2.95×10^{-4}	1.23×10^4	9.42
30	6.85×10^{-4}	3.35×10^{-4}	1.06×10^4	9.26
40	6.30×10^{-4}	3.90×10^{-4}	0.82×10^4	9.01
50	5.60×10^{-4}	4.80×10^{-4}	0.59×10^4	8.68

(c) Nickel - equilibrium pH = 3.70

Temperature °C	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	H'	$\ln H'$
20	7.60×10^{-4}	2.80×10^{-4}	1.01×10^4	9.22
30	7.90×10^{-4}	2.45×10^{-4}	1.20×10^4	9.39
40	8.05×10^{-4}	2.30×10^{-4}	1.30×10^4	9.46
50	8.10×10^{-4}	2.30×10^{-4}	1.31×10^4	9.47

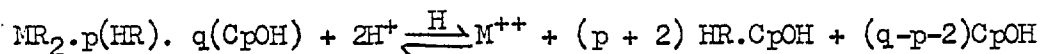
The values of H^+ in Table IV have been calculated using the equations 98-100 on pages 56 and 59. Figure VI shows graphs of $\ln H^+$ against $1/T_K$ for the three metal complexes and from these graphs values of ΔH° for the metals have been calculated, using equation 103, to be -3.9, -4.4 and +1.6 K.Cal/mole respectively for copper, cobalt and nickel.

It should be noticed that the values calculated for these heats of reaction are approximate, since, throughout the computation, activity coefficients have been assumed to be unity and unchanging. The activity coefficient of the metal ion in aqueous solution, although not absolutely known, will have remained sensibly constant throughout these experiments, except for some small change with temperature, as the total metal ion concentration has not varied significantly. However, little is known about the activity coefficients of metal solutes in organic solvents.

3.1.2 The effect of 2-ethylhexyl alcohol (capryl alcohol)

Some kinetic runs have been carried out in the presence of capryl alcohol and equilibrium studies were also carried out in the presence of this reagent, to see if it produces any significant change in the nature of the complexes.

At the concentrations of capryl alcohol used, i.e. 0.25 M to 1.0 M, the D.E.H.P. is almost entirely monomerised and hydrogen bonded to the capryl alcohol; Blake, Baes, Brown, Coleman and White¹⁰¹. The equilibrium equation therefore becomes:-



Therefore:-

$$\log m + (p+2) \log [HR] + (q-p-2) \log [CpOH] = \log H - 2pH + \log A \quad 104.$$

where A is the activity term.

By studying the effect of variation of D.E.H.P. concentration and capryl alcohol concentration on the value of m , the coefficients p & q can be evaluated. The conditions used, and the results obtained for these tests were as follows:-

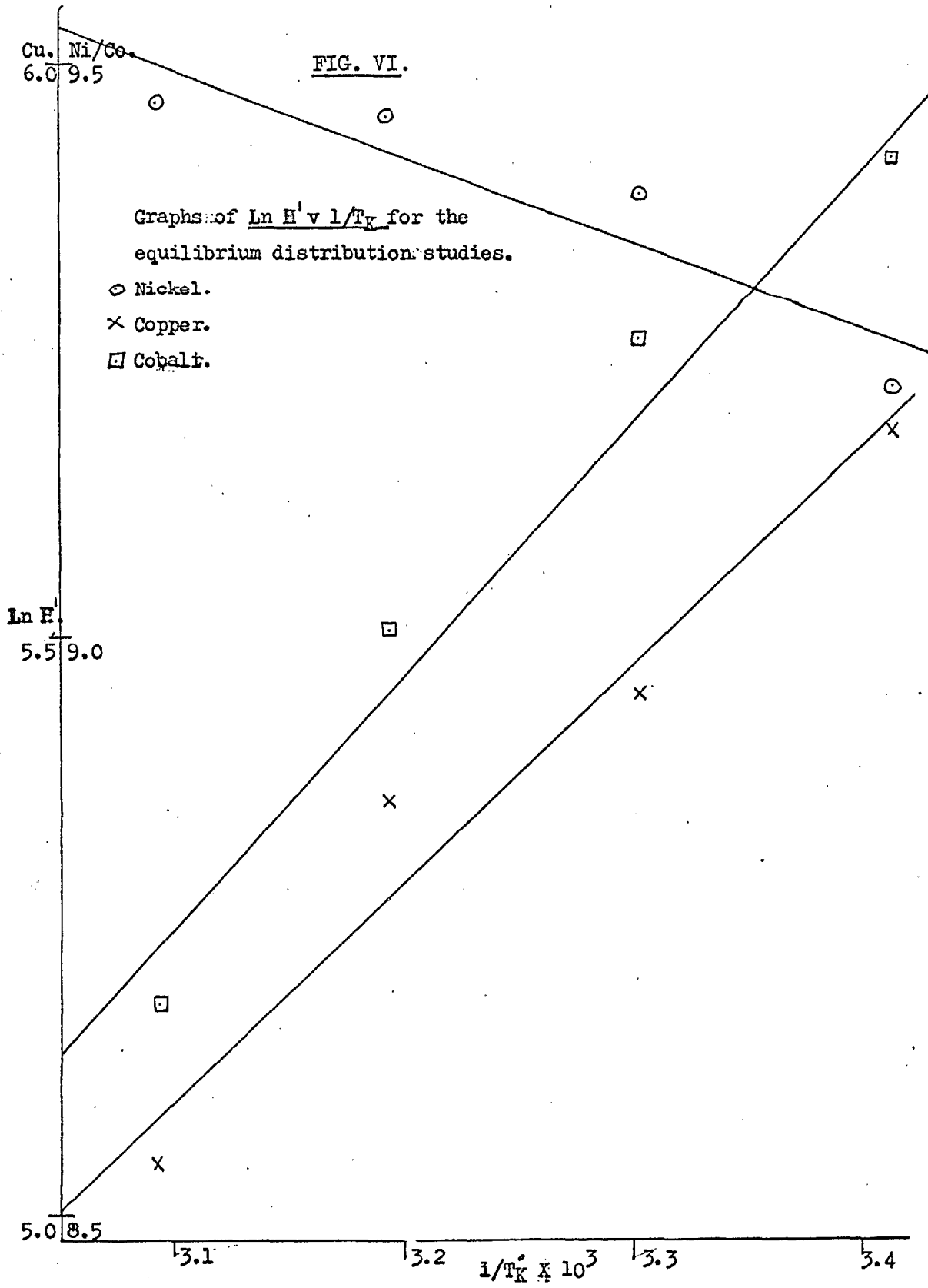


TABLE V. Equilibrium distributions at 20°C, in the presence of capryl alcohol, as a function of D.E.H.P. concentration, with total metal concentration (M_T) 10^{-3} mole/litre, and capryl alcohol concentration (C_{POH}) 0.5 mole/litre.

(a) Copper - equilibrium pH 3.00

D.E.H.P. Conc. mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	$m =$ M_a/M_o	log m
0.4	1.30×10^{-4}	7.60×10^{-4}	0.171	-0.775
0.2	4.35×10^{-4}	5.40×10^{-4}	0.805	-0.095
0.1	7.70×10^{-4}	2.20×10^{-4}	3.50	0.540
0.05	8.45×10^{-4}	9.70×10^{-5}	8.71	0.942

(b) Cobalt - equilibrium pH 3.30

D.E.H.P. Conc. mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	$m =$ M_a/M_o	log m
0.4	1.70×10^{-4}	8.30×10^{-4}	0.204	-0.690
0.2	5.60×10^{-4}	3.60×10^{-4}	1.56	0.193
0.1	9.00×10^{-4}	1.05×10^{-4}	8.56	0.932
0.05	9.65×10^{-4}	2.70×10^{-5}	35.7	1.553

(c) Nickel - equilibrium pH 3.75

D.E.H.P. Conc. mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	$m =$ M_a/M_o	log m
0.4	6.80×10^{-5}	10.10×10^{-4}	0.067	-1.174
0.2	2.45×10^{-4}	7.30×10^{-4}	0.324	-0.489
0.1	6.55×10^{-4}	3.90×10^{-4}	1.68	0.225
0.05	9.70×10^{-4}	1.23×10^{-4}	7.95	0.900

TABLE VI. Equilibrium distributions at 20°C, in the presence of capryl alcohol, as a function of capryl alcohol concentration with total metal concentration (M_t) 10^{-5} mole/litre and D.E.H.P. concentration 0.1 mole/litre.

(a) Copper - equilibrium pH 3.00

Capryl alcohol Conc. mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	$m =$ M_a/M_o
0	6.20×10^{-4}	3.85×10^{-4}	1.61
0.25	6.25×10^{-4}	3.15×10^{-4}	1.98
0.50	7.70×10^{-4}	2.20×10^{-4}	3.50
0.75	7.40×10^{-4}	2.40×10^{-4}	3.08
1.00	7.40×10^{-4}	2.40×10^{-4}	3.08

(b) Cobalt - equilibrium pH 3.50

Capryl alcohol Conc. mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole/litre	$m =$ M_a/M_o
0	6.00×10^{-4}	4.00×10^{-4}	1.50
0.25	6.00×10^{-4}	3.80×10^{-4}	1.58
0.50	6.45×10^{-4}	3.30×10^{-4}	1.95
0.75	6.35×10^{-4}	3.30×10^{-4}	1.91
1.00	6.45×10^{-4}	3.30×10^{-4}	1.95

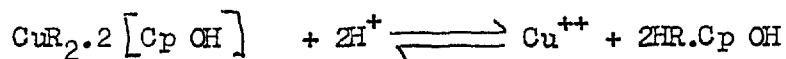
(c) Nickel - equilibrium pH = 3.85

Capryl alcohol Conc. mole/litre	Aqueous Conc. M_a mole/litre	Organic Conc. M_o mole litre	$m =$ M_a/M_o
0	5.35×10^{-4}	4.45×10^{-4}	1.20
0.25	5.90×10^{-4}	4.60×10^{-4}	1.28
0.50	6.00×10^{-4}	4.55×10^{-4}	1.32
0.75	6.00×10^{-4}	4.55×10^{-4}	1.32
1.00	6.15×10^{-4}	4.65×10^{-4}	1.32

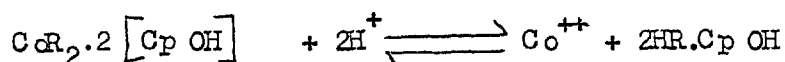
In Figure VII the results in Table V have been plotted as graphs of $\log m$ against $\log [HR]$ and the slopes of these graphs, $\left\{ \frac{\delta \log m}{\delta \log [HR]} \right\}_{pH}$, have been found to be -2.06, -2.30 and -2.47, respectively for Copper, Cobalt and Nickel. These results give values of p in equation 104 (page 61) of 0 for each metal.

From the results in Table VI it can be seen that value of the distribution coefficient reaches a constant value for capryl alcohol concentrations above 0.5 mole/litre. Hence, the value of $q-p-2$ in equation 104 is zero and thus $q = 2$. For lower concentrations than 0.5 mole/litre, $\frac{\delta \log m}{\delta \log [Cp OH]}$ is positive hence $q-p-2 < 0$ and $q < 2$. Above 0.5 mole/litre capryl alcohol the equilibrium equations for the three complexes are :-

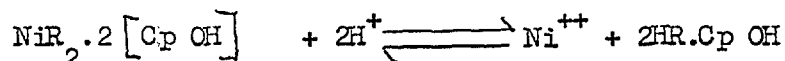
(a) Copper



(b) Cobalt

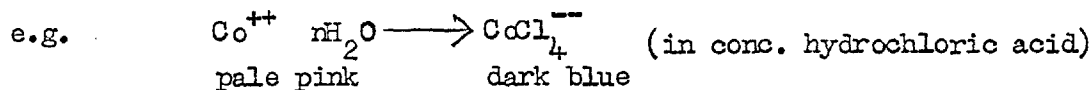


(c) Nickel



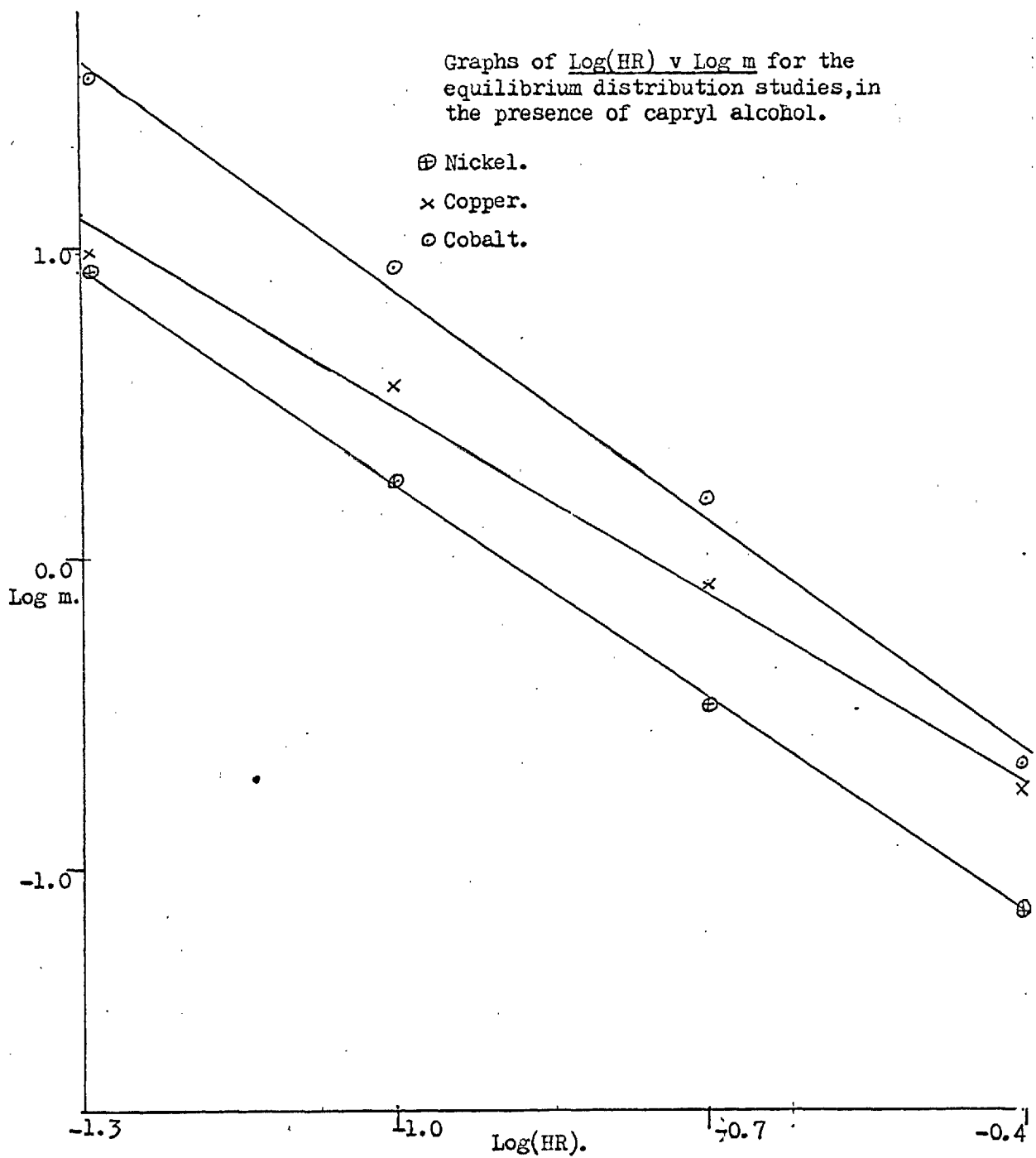
That a considerable change in structure takes place is particularly evident in the case of the cobalt complex, in view of the marked colour change of the complex; deep blue in the absence of capryl alcohol, to pale purple when it is present.

This is comparable to the change in colour of aqueous cobaltous solutions



Thus it appears that the capryl alcohol acts as a pseudo aquating agent.

FIG. VII

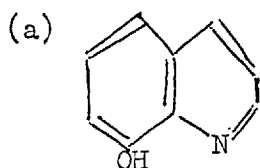


3.2 KINETIC RESULTS

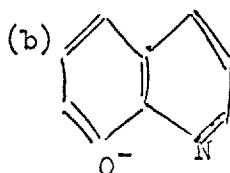
This section is divided into three main parts, part one, the results of the experiments carried out to determine the characteristics of the cell; part two, a survey of metal extraction and stripping reactions; part three, the results from the detailed study of three of those systems.

3.2.1 Determination of Cell Characteristics

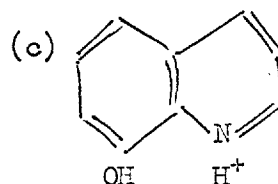
In this part of the work, a transfer system was chosen in which mass transfer occurred without chemical reaction. A suitable system is the transfer of 8-hydroxyquinoline from a buffer solution into paraffin. In aqueous solution the 8-hydroxyquinoline exists in three forms, two ionized and one un-ionized, the proportion of each form present being dependent on the pH of the solution. The structural formulae of the three forms are shown below:- (b) and (c) being the ionized forms.



Conditions: neutral

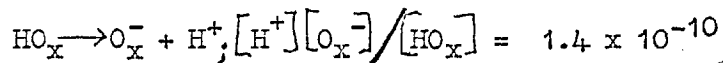
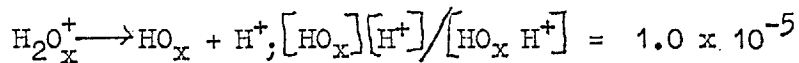


alkaline



acid

These three forms will be represented by the symbols $[HO_x]$, $[O_x^-]$ and $[H_2O_x^+]$ for (a), (b) and (c) respectively. The chemical equations for the equilibria between these three forms are given below:-



From these equations, it follows that the fraction \underline{P} of the reagent in the un-ionized form is given by:

$$P = 1 / (1 + [H^+] / 1.0 \times 10^{-5} + 1.4 \times 10^{-10} / [H^+])$$

105.

Since only the un-ionized form is extracted into paraffin, the concentration in the paraffin is proportional to \underline{P} . The maximum value of \underline{P} is at pH 7.4 when it is equal to 0.992. Under these conditions 8-hydroxyquinoline has two important characteristics:

- (a) It has a high distribution coefficient between paraffin and water, i.e. greater than 100
- (b) Extraction takes place without chemical reaction (unless there is dimerisation of the reagent in paraffin)

The phases used in the kinetic experiments were :- a saturated aqueous solution of 8-hydroxyquinoline in water, the concentration being approximately 4×10^{-3} M and purified paraffin. The aqueous phase was buffered at pH 7.4 by adding A.R. di-sodium hydrogen phosphate (85%) and A.R. sodium di-hydrogen phosphate (15%) to a total molar concentration of 0.03 M.

It was both more accurate, and convenient, to follow the kinetics of the extraction by analysing for 8-hydroxyquinoline in the organic phase. Since the transfer of the solute was in the direction aqueous to organic the concentration of solute in the organic phase was a direct and more accurate measure of the progress of the reaction in the early stages. The method of determination of the concentration in the organic phase has already been described (page 50.). The effects of the following variables on the kinetics of the reaction were determined:

- (a) Aqueous phase concentration (hence giving the order of the reaction)
- (b) Interfacial area
- (c) Stirrer speed
- (d) Temperature

3.2.1(i) Analysis of results

The organic phase concentration C_s was determined as a function of time. From the results, the value of the aqueous phase concentration, C_w , as a function of time is easily determined, knowing the volumes of the two phases, i.e.

$$C_w = C_w^0 - (C_s V_s) / V_w$$

where C_w^0 is the initial aqueous phase concentration.

If C_w^* is the aqueous phase concentration in equilibrium with the organic phase concentration, C_s , then the simplest equations which could describe the rate of extraction is :

$$d C_w / dt = - k^1 (C_w - C_w^*)^n$$

where $C_w^{\text{ss}} = C_s/m$ 106a.

Since the experiments were conducted under conditions in which $m \gg 1$ and $C_s \ll C_w$, then $C_w \gg C_w^{\text{ss}}$ and equation 106 can be written as

$$\frac{dC_w}{dt} = -k^1 C_w^n$$
 107.

For a first order reaction, as is usually found in diffusion processes, n is unity and integration of 107 gives

$$k^1 = 2.303(\Delta \log_{10} C_w / \Delta t)$$
 108.

where k^1 is related to the mass transfer coefficient K_w by

$$K_w = k^1 V_w / A$$
 108a.

where A is the interfacial area. From equation 108 a graph of $\log_{10} C_w$ against t should be a straight line of constant slope, independent of the initial aqueous phase concentration. Measured values of C_s against time together with calculated values of C_w and $\log_{10} C_w$ are given in Appendix II for all kinetic experiments on the 8-hydroxyquinoline system.

3.2.1(ii) Results

(a) Variation of initial 8-hydroxyquinoline concentration.

Experiment conditions used were:-

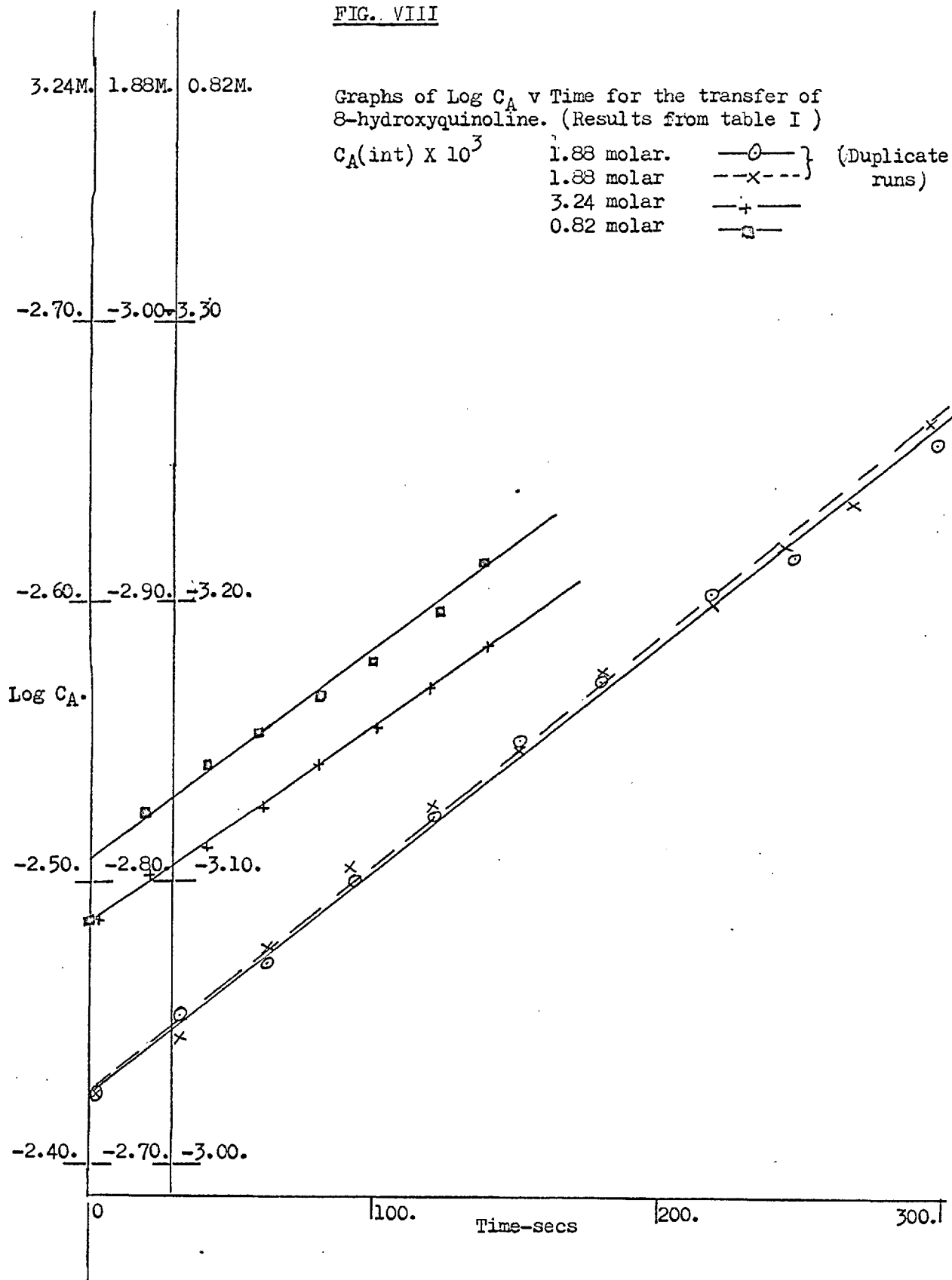
Stirring speed 60 r.p.m.
 Temperature 22.5 (295.8 K)
 Interfacial Area 8.88 cm²

Graphs of $\log_{10} C_w$ against time are shown in Fig. VIII and these are linear and parallel as expected. The values of k^1 , the rate constant, at varying levels of initial 8-hydroxyquinoline concentration are given below in Table VII.

TABLE VII.

Run No.	$C_w^0 \times 10^3$ mol/litre	$k^1 \times 10^6$ sec ⁻¹
1	1.88	27.9
2	1.88	28.9
4	0.82	29.2
5	3.24	26.9

FIG. VIII



Runs 1 and 2 have identical conditions and give rate constants identical to within $\pm 2\%$, which is adequate.

Over a four-fold change in aqueous phase 8-hydroxyquinoline concentration, k^l remains constant to within $\pm 3\%$, which establishes that the rate of mass transfer is first order with respect to aqueous phase 8-hydroxyquinoline concentration.

(b) Variation of temperature

The system variables which will change with temperature are viscosity and diffusion coefficients. Both these solution constants vary exponentially with temperature and hence it is expected that the rate of mass transfer will obey the Arrhenius equation

$$k^l = A \exp(-E_A/RT)$$

where E_A is the activation energy.

Table VIII shows values of k^l at varying temperatures. Experimental conditions used were:-

Stirring rate - 60 r.p.m.
Initial 8-hydroxyquinoline conc. (C_w) 3.24×10^{-3} mole/litre.
Interfacial Area 8.88 cm^2

TABLE VIII.

Run No.	Temp. (T) °K	$k^l \times 10^6$ sec ⁻¹	$\log_{10} k^l$	$1/T$ $\times 10^3$
5	295.8	26.9	-4.570	3.39
6	307.3	34.5	-4.462	3.26
7	320.8	43.3	-4.363	3.12
10	332.8	54.2	-4.266	3.01

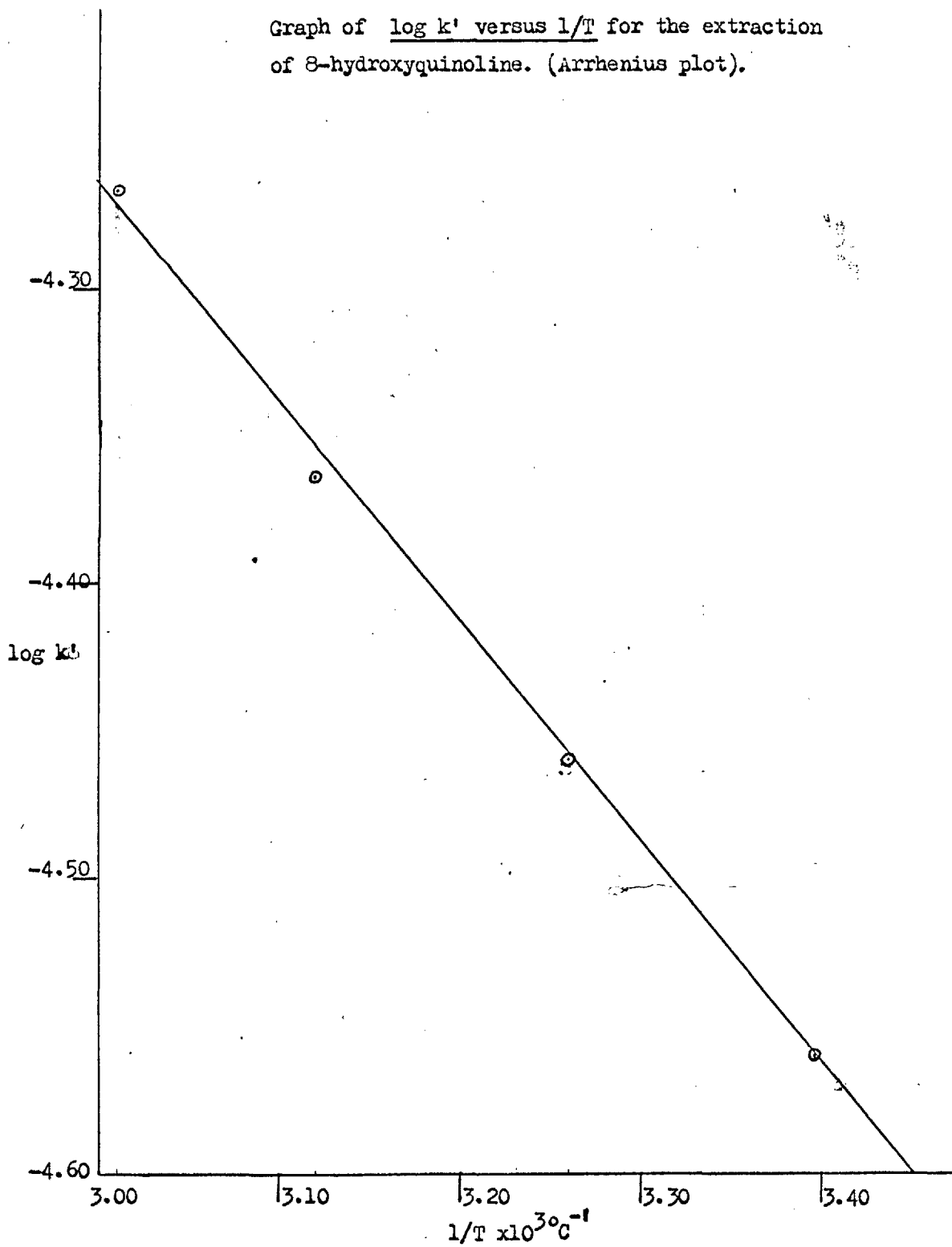
If these results fit the Arrhenius equation then a plot of $\log k^l$ against $1/T$ should be linear with a slope of $-E_A/R \times 2.303$ (where R is the gas constant). Fig. IX shows a graph of $\log_{10} k^l$ against $1/T$ and the slope gives an activation energy of 3.5 kilocalories per mole, which is a value of the order expected for a diffusion controlled reaction.

(c) Variation of stirring rate

The effect of stirring rate was studied for a twofold purpose: first, so that a comparison could be made with the empirical equations of Lewis⁶⁶ and McManamey⁹⁴ and the theoretical

FIG. IX

Graph of $\log k'$ versus $1/T$ for the extraction of 8-hydroxyquinoline. (Arrhenius plot).



equation of Olander⁹⁵; secondly, to find a method of distinguishing between a process which is controlled by the rate of transfer to or from the interface and a process which is controlled by some interfacial resistance, since it is expected that the latter will be independent of stirring rate.

Speed variations were obtained by changing the reduction gear on the synchronous motor, and a table showing rate constant as a function of stirring rate is given in Table IX.

The experimental conditions used were:-

o
 Temperature 22.5 C.
 Interfacial Area 8.88 cm²
 Initial 8-hydroxyquinoline conc. = 3.24×10^{-3} mole/litre.

TABLE IX.

Run No.	Stirring Speed r.p.m.	$k' \times 10^6$ sec ⁻¹
10	27	17.5
11	34	19.6
5	60	26.9
12	79	31.8
9	140	49.1

A graph of rate constant against stirring rate is shown in Fig. X.

The range of rate of stirring could not be increased, since at higher rates turbulence occurred at the interface and at lower rates incomplete mixing of the bulk phases occurred.

As can be seen from Fig. X, the results can be fitted to an equation of the type

$$k' = a + bS \quad 109.$$

where S is the stirring rate in revolutions per second. Values of a and b for the results in Table IX are 9.97×10^{-6} sec⁻¹ and 15.06×10^{-6} respectively. The equations of Lewis⁶⁶, McManamey⁹⁴ and Olander⁹⁵, Nos. 85, 86 and 88 respectively, all reduced to their simplest forms with two stirrers of the same dimensions and rotating at the same rate, are:

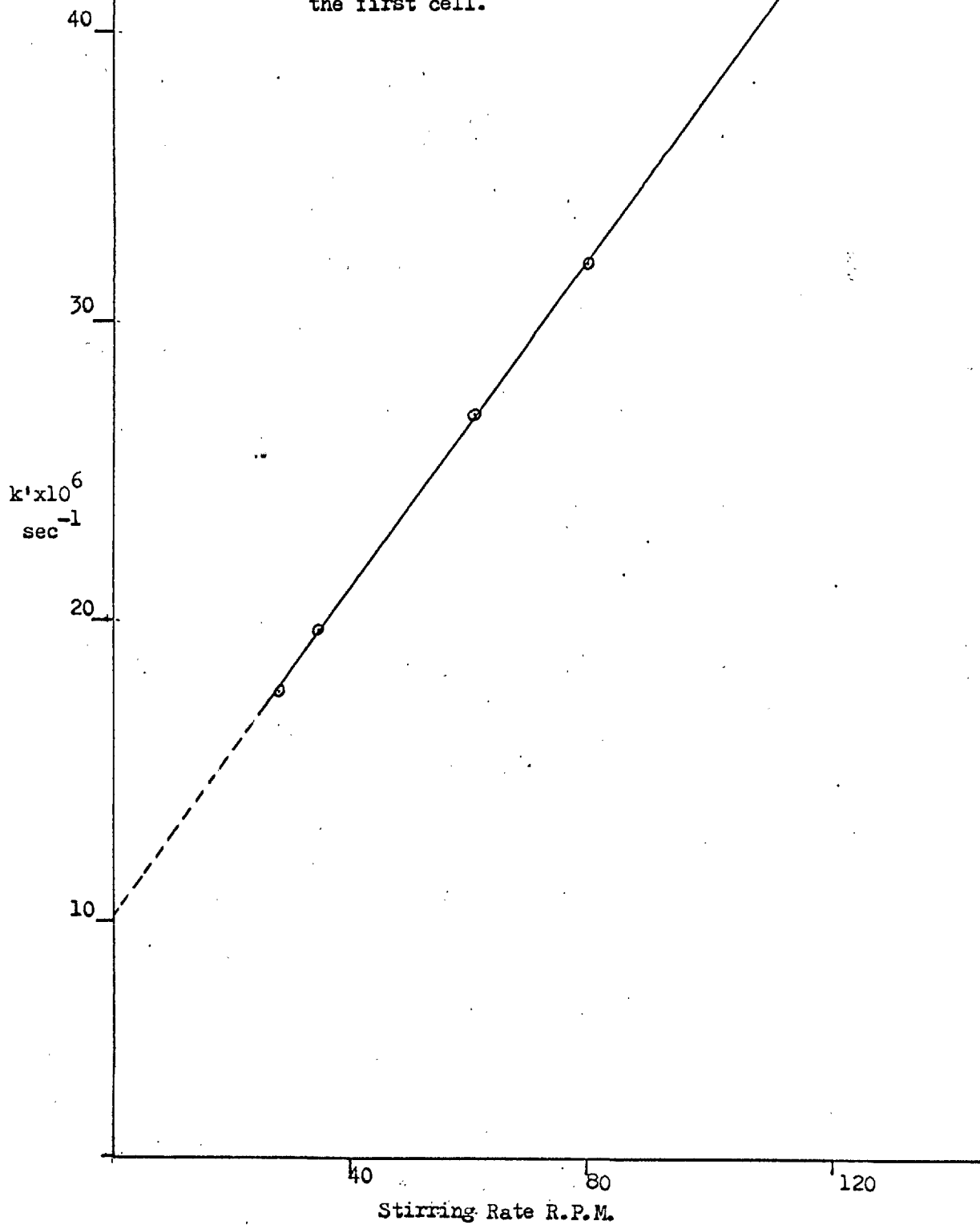
$$k' = cS^{1.65} \quad 110.$$

$$k' = dS^{0.9} \quad 111.$$

$$k' = eS^{0.5} \quad 112.$$

FIG. X.

Graph of k' versus Stirring Rate for the extraction of 8-hydroxyquinoline using the first cell.



where c, d and e are constants; The equation fitting the above results most closely is that of McManamey.

(d) Variation of Interfacial Area

According to Olander⁹⁵, the rate of mass transfer per unit area depends on the position of this interfacial area relative to the stirrer (see page 35). The rate of transfer per unit area in different parts of the interface in cells of this type has not been studied, results always being quoted in the form of overall rates of transfer divided by total area. Olander's theory indicates that this may be erroneous.

The overall rates of transfer were determined at four different interfacial areas in positions varying with respect to the cell walls and the stirrers. The values of these areas and their relative positions are given on page 39. The kinetic results for these four interfacial areas are given in Table X.

Experimental conditions used were:-

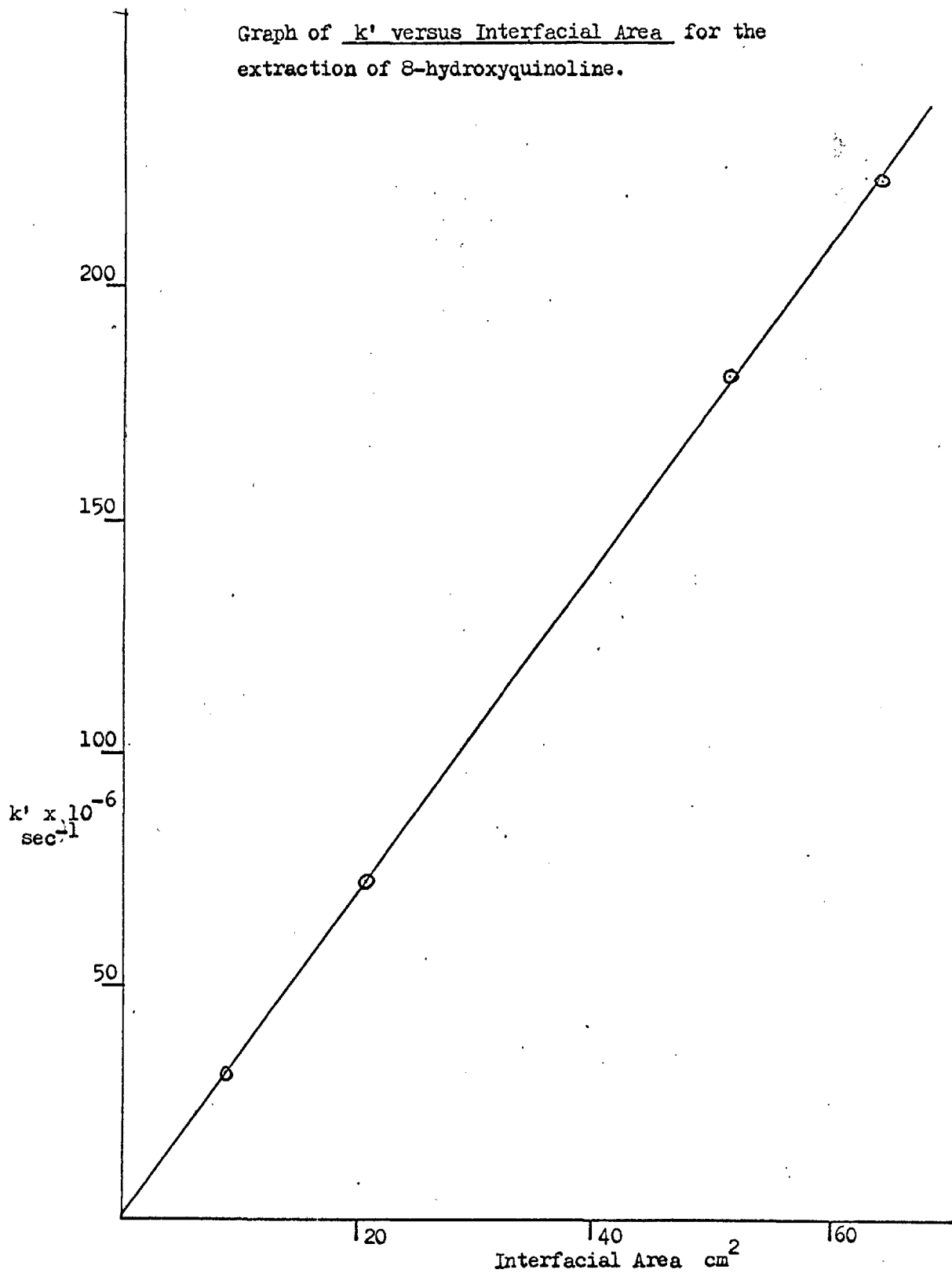
Initial 8-hydroxyquinoline conc. 3.24×10^{-3} mole/litre.
 Stirring rate 79 r.p.m.
 Temperature 22.5°C .

TABLE X.

Run No.	Interfacial Area (A) cm^2	k^1 $\text{sec}^{-1} \times 10^6$	k^1/A $\text{cm}^{-2} \text{sec}^{-1} \times 10^6$
12	8.9	31.8	3.58
22	20.1	73.5	3.65
21	51.3	179.8	3.51
23	62.6	226.3	3.62

Fig. XI shows a graph of k^1 against interfacial area which is linear and passes through the origin.

It should be noted, that the interfacial area in Runs 12 and 22 was completely within the compass of the stirring discs, i.e. the results of these runs refute Olander's⁹⁵ contention that no transfer takes place under the stirrers. In fact, the results show that rate of mass transfer per unit area is constant right across the interface and also that there are no significant end effects.

FIG XI

As there are no significant end effects at the cell wall or stirring shafts, the cell was redesigned, incorporating the same stirring unit, to make it simpler to assemble. This cell is of the form described on page 39 and shown in Fig. II. The effects of stirring rate and interfacial area were again studied in this cell. However, since no baffle was used, the interfacial area was varied by blanking off parts of the interface with discs of varying diameters fixed to the central stationary shaft. The results of these runs are shown below in Table XI.

The experimental conditions used were:-

Temperature: 22.5°C.

Initial 8-hydroxyquinoline conc. 3.24×10^{-3} mole/litre.

TABLE XI.

Run No.	Stirring Rate r.p.m.	Int. Area A. cm ²	k^1 -sec ⁻¹ x 10 ⁶	k^1/A sec ⁻¹ cm ⁻² x 10 ⁶
64	27	62.6	98.5	1.58
68	33	50.4	86.7	1.72
69	33	38.3	66.4	1.74
66	52	62.6	130.0	2.08
62	74	62.6	182.0	2.91
71	78 (co-rotated)	62.6	170.0	2.72
65	98	62.6	218.0	3.48
63	118	62.6	238.0	3.81
70	128	50.4	217.0	4.31
67	128	38.3	167.0	4.35

Fig. XII shows a graph of k^1/A against stirring rate for these results. It is noteworthy that the results obtained with 38.3 cm² and 50.4 cm² interfacial area are as good a fit to the best straight line as those obtained with 62.6 cm². The result with co-rotating stirring discs lies within the divergence of the other points from this straight line. This result is in agreement with the findings of Lewis⁶⁶ who concluded that the relative direction of rotation of the discs is not significant.

In later work, involving corrosive solutions, the metal shafts and discs were replaced by glass shafts and P.T.F.E. discs. The cell was therefore again tested by determining the rate of transfer as a function of stirring rate. The results of these

runs are shown below in Table XII.

The experimental conditions used were:-

Temperature 22.5°C.₂
 Interfacial Area ... 62.6 cm²
 Initial 8-hydroxyquinoline conc. = 3.24 x 10⁻³ mole/litre.

TABLE XII.

Run No.	Stirring Rate r.p.m.	$k^l \times 10^6$ sec ⁻¹	$k^l/A \times 10^6$ sec ⁻¹ cm ⁻²
72 (a)	24	93.2	1.49
72 (b)	47	124.0	1.97
72 (c)	69	155.0	2.47
72 (d)	94	211.0	3.36
72 (e)	118	235.0	3.77

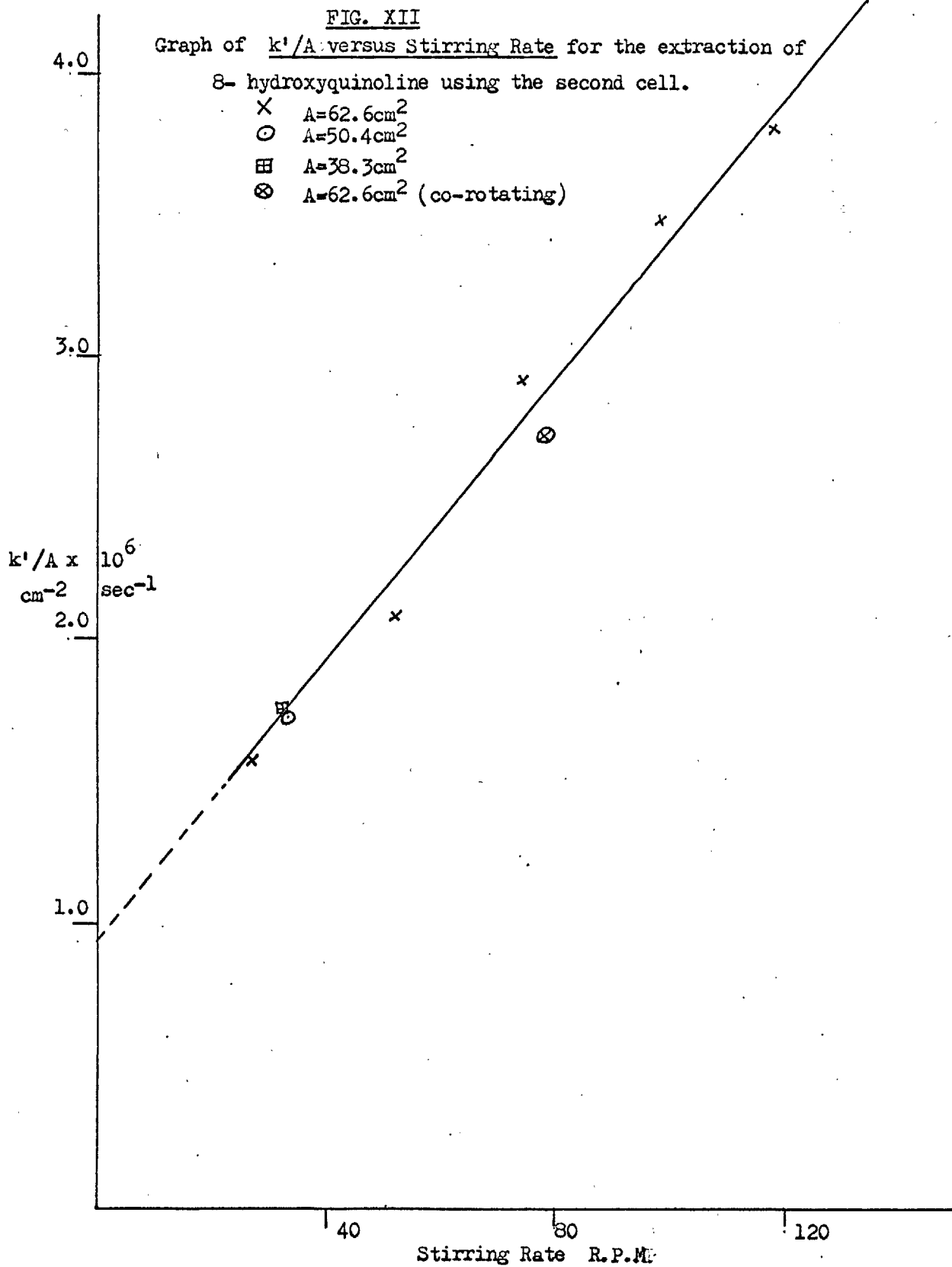
Fig. XIII shows a graph of k^l/A against stirring rate for the results in Table XII and, like the results of Tables IX and XI, a good straight line fit is obtained.

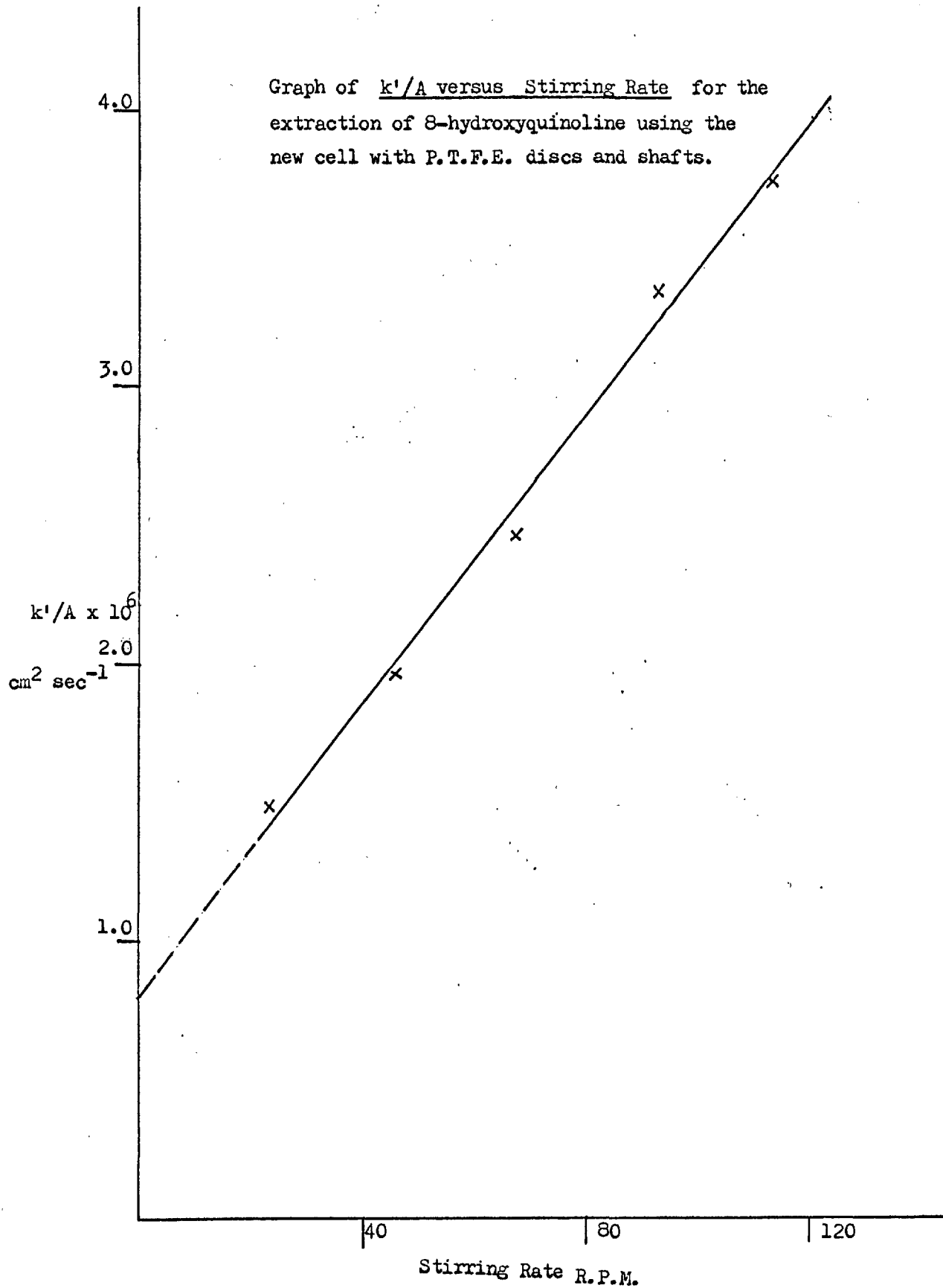
3.2.1 (iii) Conclusion from kinetic studies with 8-hydroxyquinoline

From the kinetic studies with 8-hydroxyquinoline the following conclusions for the rate of mass transfer in the absence of chemical reaction can be drawn:-

- (a) That the rate of mass transfer follows a first order law.
- (b) That the rate of mass transfer follows the Arrhenius exponential law for variation with temperature.
- (c) That the rate of mass transfer per unit interfacial area is independent of the relative position of the area between the cell walls and the centre of rotation of the discs.
- (d) That the rate of mass transfer is linearly related to the stirring rate within the range of stirring rates investigated. This law held for both cell designs used and both the metal and P.T.F.E. stirrer units.

This result is considered important since it is the basis of a method of distinguishing between systems controlled by an interfacial resistance and those controlled by transfer to or from the interface and provides a means of calculating the interfacial resistance in systems controlled partly by both mechanisms.





In the absence of an interfacial resistance, k' is related to stirring rate by the equation (see page 73)

$$k' = a + bS \quad 109.$$

k' is related to the mass transfer coefficient K_W by the equation (see page 69)

$$K_W = k'V_w/A \quad 108a.$$

Elimination of k' leads to the following relationship between K_W and stirring speed S

$$K_W = (V_w/A)(a + bS) \quad 114.$$

which gives $K_W = a' + b'S$ 115.

For 8-hydroxyquinoline, the values of a' , b' and K_W (at $S = 1 \text{ rev. sec}^{-1}$) are, for the three cell modifications, given in Table XIII.

TABLE XIII.

Cell Type	$a' \times 10^4$ cm sec ⁻¹	$b' \times 10^4$ cm	$K_W(60 \text{ rpm}) \times 10^4$ cm sec ⁻¹
First cell, metal stirrers	2.66	4.00	6.66
Modified cell, metal stirrers	1.79	4.40	6.19
Modified cell, P.T.F.E. stirrers	1.97	4.22	6.19

In the presence of an interfacial resistance, the concept of additivity of resistances (page 13) leads to:-

$$1/K = 1/K_W + 1/K_i \quad 116.$$

where K_W is the coefficient of mass transfer in the absence of interfacial resistance and K_i the coefficient of interfacial mass transfer. Substitution of 114 in 116 gives, for a system having interfacial resistance,

$$1/K = 1/(a' + b'S) + 1/K_i \quad 117.$$

Providing $b' \gg a'$, at the higher values of S used, then

$$1/K = 1/b'S + 1/K_i \quad 118.$$

Thus there is a linear relation between $1/K$ and $1/S$, with an intercept at $1/S = 0 (S = \infty)$ of $1/k_i$. This analysis will be used later in this thesis for interpreting the results for systems believed to have interfacial resistances.

3.2.2 Survey of Extraction System

A survey of a series of metal-organic systems was carried out in order to make a selection of systems whose rates of transfer were significantly slower than that of 8-hydroxyquinoline.

During this survey four different organic extractants were used, viz:- naphthenic acid, di-2-ethylhexyl-phosphoric acid, tri-butyl phosphate and tri-iso-octylamine. The metal ions studied were:- Cu^{++} , Ni^{++} , Zn^{++} , Co^{++} , Fe^{+++} , Al^{+++} and UO_2^{++} .

Some rates of transfer in both directions were determined, and conditions from one system to another were kept constant to as great a degree as possible. In all cases the concentration of extractant in the organic phase and buffer in the aqueous phase were kept high compared with the metal ion concentrations present. Conditions were chosen so that the extraction under study went almost to completion at equilibrium. Under these conditions, providing $k_w \approx k_s$.

$$1/K_w = 1/k_w$$

119.

One run on each system was conducted and it was continued to at least 60% of completion. Experimentally determined values of K (the overall mass transfer coefficient) were obtained by plotting $\log C_w$ against time ($\log C_s$ against time for stripping reactions).

In the case of tri-iso-octylamine, 10% capryl alcohol was added to the organic phase to prevent third phase formation. For the extraction of CoCl_4^{--} into tri-iso-octylamine and $\text{UO}_2(\text{NO}_3)_2$ into tri-butyl phosphate, the aqueous buffer was replaced by 6M HCl and 5.5M HNO_3 respectively in order to obtain high distribution coefficients.

The 0.2M ammonium acetate/ammonia solutions giving pH's of 7.0 and 8.2 for extractions of copper and nickel respectively into D.E.H.P. and naphthenic acid were not strictly buffer solutions, but were used, firstly, to prevent metal hydroxide precipitation and, secondly, to provide aqueous solutions of the same

total ionic strength as those using buffer solutions.

Table XIV shows the results of these runs; the value of K_1 for oxine (8-hydroxyquinoline) at the same stirring speed and temperature is included for comparison.

Experimental conditions used for these runs were:-

Temperature 22° 5°C.
 Stirrer Speed 79 r.p.m.
 Extractant Concentration 0.2M
 Buffer Concentration 0.2M
 Initial metal ion concentration 0.02M approx.
 (this varied from 0.035 to 0.010)

TABLE XIV.

Metal	Direction of Transport	Conc of Aqueous Buffer	Conc of Organic Reagent	$K_1 \times 10^4$ cm sec ⁻¹
Oxine	Aq → Par	0.03M Phosphate pH 7.4	-	7.60
Cu ⁺⁺	Aq → Nap/Par	0.2M Acetate pH 8.2	0.2M Nap	15.20
Ni ⁺⁺	Aq → Nap/Par	0.2M Acetate pH 8.2	0.2M Nap	32.1
Ni ⁺⁺	Nap/Par → Aq	0.2M CH ₂ CICOOH pH 2.0	0.2M Nap	1.35
Co ⁺⁺	Nap/Par → Aq	0.2M CH ₂ CICOOH pH 2.0	0.2M Nap	2.00
Zn ⁺⁺	Nap/Par → Aq	0.2M CH ₂ CICOOH pH 2.0	0.2M Nap	1.39
UO ₂ ⁺⁺	Aq → DEHP/Par	0.2M CH ₂ CICOOH pH 2.0	0.2M D.E.H.P.	4.75
Fe ²⁺⁺	Aq → DEHP/Par	0.2M CH ₂ CICOOH pH 2.0	0.2M D.E.H.P.	2.04
Cu ⁺⁺	Aq → DEHP/Par	0.2M Acetate pH 7.0	0.2M D.E.H.P.	29.6
Ni ⁺⁺	Aq → DEHP/Par	0.2M Acetate pH 7.0	0.2M D.E.H.P.	17.8
Cu ⁺⁺	DEHP/Par → Aq	0.2M CH ₂ CICOOH pH 2.0	0.2M D.E.H.P.	1.71
Ni ⁺⁺	DEHP/Par → Aq	0.2M CH ₂ CICOOH pH 2.0	0.2M D.E.H.P.	2.14
Co ⁺⁺	Aq → T.I.O./Par	6M HCl	0.2M T.I.O.+ 10% CpOH	34.3
UO ₂ (NO ₃) ₂	Aq → T.B.P/Par	5.5M HNO ₃	10.2M T.B.P.	2.35

(The abbreviations used above were Aq = aqueous phase; Par = paraffin phase; Nap = naphthenic acid; D.E.H.P. = di-2-ethylhexyl phosphoric acid; CpOH = capryl alcohol; T.I.O. = tri-iso-octylamine; and T.B.P. = tri-butyl-phosphate.)

From Table XIV two main groups of reactions appeared to have appreciably slower mass transfer rates than that for the transfer of 8-hydroxyquinoline from aqueous solution into paraffin; the stripping of cobalt, nickel and zinc from naphthenic acid, and the stripping of copper and nickel from D.E.H.P. Other slow

reactions were the extraction of uranium nitrate into T.B.P. and the extraction of ferric iron and aluminium into D.E.H.P. An attempt was also made to measure the rate of stripping of beryllium from D E.H.P. but this was found to be so slow that no value could be put to it. The order of the rate was approximately 0.1% in six hours. Because of this extreme slowness it was decided that further study of this system would be too time-consuming. The same applied to the stripping of aluminium from D.E.H.P.

Before choosing systems for more detailed study it is necessary to ascertain whether the slowness, compared with 8-hydroxyquinoline, is due to the difference in diffusion coefficient between that for 8-hydroxyquinoline in buffer solution and that for the metal ions in naphthenic acid and D.E.H.P., or due to the effect of some interfacial resistance. This was determined by calculating an approximate mass transfer coefficient based on the mass transfer coefficient for 8-hydroxyquinoline, and McManamey's correlation. Assuming McManamey's correlation, i.e.

$$K_{\alpha} = \alpha \sqrt[1.9]{Sc_{\alpha}}^{-0.37} (Re_{\alpha})^{0.9} (1 + \eta_{\beta} Re_{\beta} / \eta_{\alpha} Re_{\alpha}) \quad 121.$$

where α and β refer to the phases from which and into which transfer takes place respectively.

When both discs rotate at the same speed, and the same stirring speed is considered for 8-hydroxyquinoline and the system to be compared, then:-

$$K = K_{ox} \left(\sqrt[1.9]{Sc}^{-0.39} / \sqrt[1.9]{Sc_{ox}}^{-0.39} \right) \text{ for } K \text{ aqueous} \rightarrow \text{paraffin} \quad 122a.$$

$$K = K_{ox} \left(\sqrt[1.9]{Sc}^{-0.39} / \sqrt[1.9]{Sc_{ox}}^{-0.39} \right) \left(\sigma_{aq} / \sigma_{par} \right) \text{ for } K \text{ paraffin} \rightarrow \text{aqueous} \quad 122b.$$

where the subscript 'ox' refers to 8-hydroxyquinoline.

The values of K calculated above and the values of K found experimentally are given in Table XV for the two main groups of apparently slow systems.

TABLE XV.

System		K(exp)(table XIV) x 10 ⁴	K (calc) x 10 ⁴
Metal	Transfer	cm. sec ⁻¹	cm. sec ⁻¹
Oxine	Aq → Par	7.60	7.60
Ni ⁺⁺	Nap/Par → Aq	1.35	5.75
Co ⁺⁺	Nap/Par → Aq	2.00	5.82
Cu ⁺⁺	D.E.H.P/Par → Aq	1.71	4.98
Ni ⁺⁺	D.E.H.P/Par → Aq	2.14	5.05

As can be seen from this table, the values calculated are not as low as those measured experimentally, and it would appear that some interfacial resistance is present.

Of the two groups the systems involving stripping from D.E.H.P. appeared to have certain advantages for detailed study:-

- (a) D.E.H.P. can be more easily obtained in a pure state than naphthenic acid.
- (b) During stripping of a metal from naphthenic acid, a small quantity of the organic phase was dispersed in the aqueous phase. As the run progressed, bubbles of the aqueous phase became trapped in thin skins of organic phase near the interface. The metal ions which were transferred to these bubbles did not appear in the main body of the solution which was analysed; consequently, the rate could not be determined. During stripping from D.E.H.P., much smaller quantities of the organic phase were dispersed and there was no trapping of the solute.
- (c) It has been established that D.E.H.P. is dimerised in paraffin¹⁰². It is expected that naphthenic acid, like other carboxylic acids, will also be dimerised, but no experimental evidence has been obtained.
- (d) There is some doubt as to whether the metal naphthenate is in true solution in paraffin. If it is not, it may prove difficult to obtain reproducible results, also the interpretation of results would be complicated.

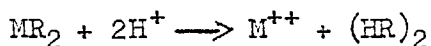
For these reasons it was decided to study the stripping of copper, nickel and cobalt from D.E.H.P., and the feature of primary interest was to be the interfacial resistance.

3.2.3 Kinetics of stripping of copper, nickel and cobalt from di-(2-ethylhexyl)-phosphoric acid

3.2.3(i) Solution Preparation and Experimental Techniques

The method of preparation of the metal organic solutions and the basic experimental techniques used in rate determinations have already been described on pages 44 and 45 respectively. However, for this part of the work certain modifications of the experimental techniques, used in the 8-hydroxyquinoline studies and general systems' survey, were made.

The determination of the variation of transfer rate with stirring rate has already been shown to be the key to this part of the work (page 81). To prevent the work being too time-consuming, the rate of stripping at five different stirring rates was determined during each run. Rapid speed changes were made by the technique described on page 41. The time of stripping at each stirring rate was kept short, as a result of which the driving force for stripping remained sensibly constant throughout each constant stirring rate period. The concentration of organic reagent was maintained approximately constant by using a ten-fold excess. As described on page 45, the pH of the aqueous phase was continually monitored and adjusted to a constant value by the addition of small quantities of concentrated sulphuric acid from a syringe. This was necessary as buffered solutions were not used for the stripping and the transfer of metal ions from the organic to the aqueous phase involves the counter-current transfer of H^+ from the aqueous to the organic phase, i.e.



3.2.3(ii) Analysis of Results

- (a) Determination of the Mass Transfer Coefficient, K .
The rate of stripping, R , is defined by the equation

$$R = dC_s/dt \quad 123.$$

(where C_s is the organic phase concentration).

A mass balance for the metal lead to

$$C_s = C_s^0 - C_w V_w / V_s \quad 124.$$

(where C_w is the aqueous phase concentration).

Differentiating equation 124 and substituting in 123 gives

$$R = (dC_w/dt) V_w / V_s \quad 125.$$

and since equal phase volumes were used in the experiments, equation 125 simplifies to

$$R = dC_w/dt \quad 126.$$

The value of dC_w/dt was determined from the measured values of C_w obtained during each twenty-minute sampling period. Five samples were taken for each stirrer speed at five-minute intervals. From the analyses of the five samples the value of dC_w/dt was determined using the technique of linear regression by least squares.

The general expression for the regression coefficient α , for the best straight line $(y-\bar{y}) = \alpha(x-\bar{x})$ through a series of values of a dependent variable, y , for values of an independent variable, x , is given by the equation:-

$$\alpha = \left[\frac{n \sum yx - \sum x \sum y}{n \sum x^2 - (\sum x)^2} \right] \quad 127.$$

$(\bar{y} \text{ \& } \bar{x})$ are the mean values of y and x , and n the number of terms.

The accuracy of the regression coefficient is defined by the standard error of the coefficient, which is the square root of the variance of the regression, δ^2 . This variance is given by the equation

$$\delta^2 = \left[\frac{\sum (y-\bar{y})^2 / \sum (x-\bar{x})^2 - \alpha^2}{n-2} \right] \quad 128.$$

The 95% confidence limits of the regression coefficient, as a percentage of the regression coefficient, are given by

$$\pm 200 \left\{ \left[\frac{\sum (y-\bar{y})^2 / \alpha^2 \sum (x-\bar{x})^2}{n-2} - 1 \right] / (n-2) \right\}^{1/2} \quad 129.$$

If we designate y by the five analyses C_{w0} , C_{w5} , C_{w10} , C_{w15} and C_{w20} at values of x of 0, 5, 10, 15 and 20 minutes and substitute these in equation 127, we obtain the following relationship for the slope R :-

$$R = \left\{ \left[2(C_{w20} - C_{w0}) + (C_{w15} - C_{w5}) \right] / 3 \right\} \times 10^{-3} \text{ mol/litre sec.} \quad 130.$$

Although the value of C_{w10} does not appear in the equation for R , it does affect its statistical accuracy.

The driving force for the mass transfer is given by $(C_s - C_w/m)$ where m is the distribution coefficient. A mass balance for the solute leads to

$$C_s = C_s^0 - C_w - \sum v C_w/V \quad 131.$$

for equal phase volumes \underline{V} ;

Where $\sum v C_w$ represents the molar quantity of the metal removed as samples and replaced by distilled water. The mass transfer coefficient, \underline{K} , is defined by

$$K = [V.R] / [A (C_s - C_w / m)] \quad 132.$$

Substitution of equations 126 and 131 in equation 132 gives:-

$$K = [v d C_w / dt] / [A(C_s^0 - C_w \{1 + 1/m\} - \sum v C_w / V)] \quad 133.$$

This equation assumes that the value of the driving force remained constant over a single determination of (dC_w/dt) , i.e. at any one particular speed. This assumption is valid since the greatest change in the driving force encountered was $\pm 2\frac{1}{2}\%$ of its mean value during that rate determination.

The values of the distribution coefficient, \underline{m} , used for calculation of the mass transfer coefficients, were determined from the equations on page 59; the values of $\log \gamma$ (metal ions) being calculated from the equation¹⁰⁴

$$\log \gamma = -2.016(4C_w + 1.5H^+)^{\frac{1}{2}} / [1 + (4C_w + 1.5H^+)^{\frac{1}{2}}] \quad 134.$$

The accuracy of determination of the mass transfer coefficient is dependent on the accuracy of determination of dC_w/dt . The statistical formula for the confidence limits of a regression coefficient has been given on page 87. From this formula, these limits could be calculated for each and every one of the rates determined. However, this was considered to be too time-consuming and an approximation for the average percentage error in the rate determinations has been derived in the following manner.

For \underline{P} rate determinations, the mean % error is given by $(1/P)[\text{Sum of the percentage errors}]$ as given by equation 131. However, a good approximation is to find the mean variance of regression $\underline{\delta}^2$ and the mean regression coefficient $\underline{\alpha}$ and from them to calculate the mean fractional 95% confidence limit $\underline{\bar{c}}$ from the equation

$$\bar{c} = 2\sqrt{\delta^2} / \alpha \quad 135.$$

If $\underline{\Omega}$ is the sum of a number of factors from \underline{P} rate determinations, then

$$\delta^2 = \left\{ \sum_{i=1}^{\Omega} (y_i - \bar{y})^2 \right\} / \left\{ \sum_{i=1}^{\Omega} (x_i - \bar{x})^2 - \Omega \alpha^2 \right\} / P(n-2) \quad 136.$$

if $\sum (x - \bar{x})^2$ is the same for each rate determination.

In terms of the rate determinations, $n = 5$, $y = C_w$, $x = \text{time}$ (in seconds) and $\alpha = R$, substituting these into equation 137 and then combining 137 and 135 gives:-

$$\bar{c} = \left[\frac{\Omega \sum (C_w - \bar{C}_w)^2}{(9 \times 10^5) - \Omega R^2} \right]^{1/2} \frac{2P}{\Omega R} \quad 138.$$

From all the rate determination data collected, which are to be found in Appendix III (a-c), the average error of the rate determinations, \bar{c} , was calculated to be ± 0.10 , ± 0.06 and ± 0.10 respectively for the stripping of copper, nickel and cobalt.

(b) Variation of Mass Transfer Coefficient with Stirring Rate

On page 81 it was proposed that the concept of additivity of resistances be used in studying the mass transfer of a species in the presence of an interfacial resistance.

This concept gives the equation:

$$1/K = 1/K_w + 1/K_c \quad 140.$$

where K is the overall mass transfer coefficient, K_w the mass transfer coefficient in the absence of any interfacial resistance and K_c the mass transfer coefficient for the interfacial resistance. It has been shown for 8-hydroxyquinoline that the relationship between K_w and stirring rate, S , is of the linear form:

$$K_w = a + bS \quad 141.$$

Substituting this equation into equation 140 gives

$$1/K = 1/(a + bS) + 1/K_c \quad 142.$$

At high stirring rates, S , and if b and K_c are constant, this approximates to

$$1/K = 1/bS + 1/K_c \quad 143.$$

which gives a linear relationship between $1/K$ and $1/S$.

However, while the influence of S on K was being determined experimentally, the metal concentrations in the two phases were changing. It has already been shown (pages 26-28) that, when diffusion of several species is involved, the coefficient

of mass transfer through the two solutions, \underline{bS} , is dependent on the concentrations of all the species. Thus \underline{b} was not constant during an experiment in which \underline{K} as a function of \underline{S} was determined. Also, one purpose of this research was to study how the concentrations of the species influenced the coefficient for mass transfer across the interface, $\underline{K_c}$. Therefore it would be inconsistent to assume that $\underline{K_c}$ is not also concentration dependent. Thus $\underline{K_c}$ may not be assumed to remain constant during a series of values of \underline{S} .

Although there is, therefore, not an exact linear relationship between $\underline{1/K}$ and $\underline{1/S}$, the changes in concentration were sufficiently small, in most experiments, to give only slight changes in \underline{b} and probably $\underline{K_c}$. On this basis the data for \underline{K} can be treated as follows:-

A linear relation is assumed between $\underline{1/K}$ and $\underline{1/S}$ and first approximations are found for values of $\underline{1/K_c}$ and $\underline{1/b}$. Corrections to $\underline{1/K_c}$ from the theoretical relation between $\underline{1/b}$ and the solution concentrations can then be made and these corrected values of $\underline{K_c}$ are then interpreted in terms of the mean concentrations of species existing during the run. When this analysis was carried out on a few results it became apparent that, in general, when $\underline{1/b}$ was large, the correction was too large to give a determination of $\underline{1/K_c}$ with sufficient precision, and when $\underline{1/b}$ was small, the correction to $\underline{K_c}$ was negligible anyway.

As little improvement in the value of the results was obtained for a lengthy numerical calculation, the procedure was not continued. However, it was possible to account qualitatively for a few results which at first appeared to be anomalous.

The details of the method used to obtain the more accurate values of $\underline{1/K_c}$ and an estimate of the accuracy of these values are as follows:-

The best straight line through the results plotted as $\underline{1/K}$ versus $\underline{1/S}$ gives the values of $\underline{1/K_c}$ and $\underline{1/b}$; the final corrected value required is $\underline{1/K_c}$. Consider the results for the maximum and minimum stirring speeds $\underline{S_1}$ and $\underline{S_2}$ respectively. The corresponding values of \underline{K} experimentally determined, are $\underline{K_1}$ and $\underline{K_2}$ and the corresponding values of \underline{b} are $\underline{b_1}$ and $\underline{b_2}$, then

$$\underline{1/K_2} = \underline{1/K_c} + \underline{1/b_2 S_2} = \underline{1/K_c} + \underline{1/b_2 S_2} \quad 137.$$

$$\underline{1/K_1} = \underline{1/K_c} + \underline{1/b_1 S_1} = \underline{1/K_c} + \underline{1/b_1 S_1} \quad 137(a)$$

$$\text{Therefore, } \frac{1}{K_c^{\dagger}} - \frac{1}{K_c} + \frac{1}{b} S_2 = \frac{1}{b_2} S_2 \quad 139.$$

$$\frac{1}{K_c^{\dagger}} - \frac{1}{K_c} + \frac{1}{b} S_1 = \frac{1}{b_1} S_1 \quad 139a.$$

If the fractional change in the value of 'b' from S_1 to S_2 is E , then $b_2 = b_1 (1 + E)$.

Substituting 139 and 139a and rearranging gives

$$\frac{1}{K_c} = \frac{1}{K_c^{\dagger}} + E \left(\frac{1}{b} \right) \left[S_2 (E + 1) - S_1 \right] \quad 144.$$

Therefore the fractional correction to $\frac{1}{K_c^{\dagger}}$, $\frac{E^{\dagger}}$, $\left[\frac{1}{K_c} = \left(\frac{1}{K_c^{\dagger}} \right) (E^{\dagger} + 1) \right]$ is given by

$$E^{\dagger} = E \left(\frac{1}{b} \right) / \left(\frac{1}{K_c} \left[S_2 (E + 1) - S_1 \right] \right) \quad 144a.$$

The value of E in this equation can be determined in the following manner:

The general form of the relationship between K_w and the concentrations of species present was given on page 27. Putting this equation in more specific terms, for the stripping of metal ions from D.E.H.P. with sulphuric acid, gives the equations (145-147) where $K_w = b$, if individual mass transfer coefficients at unit stirring rate (rev/sec.) are used.

For copper

$$\frac{\sqrt{K_w} \delta_{Cu^{++}} \left[(C_s - C_w/m) \frac{1}{k_w} + \frac{C_w}{K_w} \right] \left[C_c/2K_w + (C_s - C_w/m) 5/2k_c \right]^{5/2}}{\left[C_s/K_w - (C_s - C_w/m) \frac{1}{k_s} \right] \left[C_D/K_w - 2(C_s - C_w/m) / k_D \right]^2} = 3.16 \times 10^2 \quad 145.$$

For cobalt

$$\frac{\delta_{Co^{++}} \left[(C_s - C_w/m) \frac{1}{k_w} + \frac{C_w}{K_w} \right] \left[C_c/2K_w + (C_s - C_w/m) 2/k_c \right]^2}{\left[C_s/K_w - (C_s - C_w/m) \frac{1}{k_s} \right] \left[C_D/K_w - (C_s - C_w/m) 2/k_D \right]^2} = 1.10 \times 10^4 \quad 146.$$

For nickel

$$\frac{\sqrt{K_w} \delta_{Ni^{++}} \left[(C_s - C_w/m) \frac{1}{k_w} + \frac{C_w}{K_w} \right] \left[C_c/2K_w + (C_s - C_w/m) 5/2k_c \right]^{5/2}}{\left[C_s/K_w - (C_s - C_w/m) \frac{1}{k_s} \right] \left[C_D/K_w - 2(C_s - C_w/m) / k_D \right]^2} = 1.26 \times 10^4 \quad 147.$$

Legend

γ is the aqueous metal ion activity coefficient, as given by equation 134 (page 88).

C_s is the organic metal concentration.

C_w is the aqueous metal concentration.

C_c is the D.E.H.P. concentration, in terms of the monomer.

C_D is the hydrogen ion concentration.

k_s , k_w , k_c and k_D the respective individual phase mass transfer coefficients.

K_w the overall mass transfer coefficient (in the absence of interfacial resistance).

m , the distribution coefficient for the metal between the aqueous and organic phase; values of m are given on page 59.

Using these equations the overall mass transfer in the absence of interfacial resistance can be calculated, provided that values of individual coefficients for the species can be determined.

Values of the individual mass transfer coefficients of the individual species can be calculated using McManamey's correlation and the value of the mass transfer coefficient for 8-hydroxyquinoline given on page 81.

The equation for these calculations using McManamey's correlation, simplified for a system with stirrers rotating at equal speeds, is given by equation 122 (page 84). To use this formula for the determination of mass transfer coefficients, values of viscosities and diffusion coefficients are required.

The viscosities have been determined experimentally and the results are given on pages 132-133. The diffusion coefficients have been calculated using Einstein's formula (90a), page 47, for organic solutions and equation 90 (page 47) for aqueous solutions. Some values of diffusion coefficients in organic solution have been determined experimentally (page 134) using the method described on page 48; these experimental values serve as a check on the application of Einstein's formula.

In Tables XVI and XVII below, calculated values of individual mass transfer coefficients at unit stirring rate (sec^{-1}) are shown for the species used in equations 145-147 (page 91). It will be seen that, for the organic solutions, the variation of viscosity with both metal and extractant concentration gives variations in mass transfer coefficients.

TABLE XVI. Mass transfer coefficients in water

Species	Individual mass transfer coefficient, \underline{k} , @ 1 rev/sec. $\times 10^4$ cm. sec $^{-1}$
H ₂ SO ₄	11.40
CuSO ₄	7.69
NiSO ₄	7.62
CoSO ₄	7.62

TABLE XVII. Mass transfer coefficients in D.E.H.P. solutions

Metal	D.E.H.P. conc M	$k(\text{metal complex}) @ 1 \text{ rev/sec}$ $\times 10^4$ (cm. sec $^{-1}$)	$k(\text{D.E.H.P.}) @ 1 \text{ rev/sec.}$ $\times 10^4$ cm. sec $^{-1}$
Copper	0.4	3.81	4.28
"	0.2	4.14	4.64
"	0.1	4.46	5.01
"	0.05	4.55	5.08
"	0.1(0.5 C _p OH)	3.68	4.06
Nickel	0.4	3.77	4.24
"	0.2	3.95	4.44
"	0.1	4.18	4.68
"	0.05	4.26	4.84
"	0.1(0.5 C _p OH)	3.66	4.06
Cobalt	0.4	2.86	3.13
"	0.2	3.19	3.50
"	0.1	3.29	3.59
"	0.05	3.41	3.73
"	0.1(0.5 C _p OH)	3.88	4.23

These calculated values of individual mass transfer coefficients can be used to determine overall mass transfer coefficients in the absence of interfacial resistance (\underline{b} in equation 143 since \underline{K}_w at 60 r.p.m. = \underline{b}) and the fractional change in \underline{b} , \underline{E} (equation 144), due to variation of \underline{C}_S and \underline{C}_W (equations 145-147) during a kinetic run. The absolute values of \underline{b} determined will not have a high degree of accuracy, since McManamey's correlation is only an

average empirical relationship for a number of transfer systems. However, the accuracy of determination of the change in \underline{b} , viz. \underline{E} , should be higher.

The accuracy of the experimental determinations of the uncorrected values of the interfacial resistance, $(1/K_c)$, is determined by the experimental accuracy of the determination of values of overall mass transfer coefficient, $(1/K)$, and the relative levels of $1/b$ and $1/K_c$ (equation 143).

If \bar{c} is the average fractional error in \underline{K} (95% confidence limits 2δ), then the variance δ_1^2 is given by

$$\delta_1^2 = (\bar{c}K/2)^2 \quad 148$$

If δ_1^2 is the variance of \underline{K} , then the variance of $1/K$, δ^2 , is given by

$$\delta^2 = (1/K^4)\delta_1^2$$

Therefore

$$\delta^2 = (\bar{c}/2K)^2 = (\bar{c}^2/4) (1/K)^2 \quad 149$$

For a best straight line, $y = \alpha x + \beta$, for experimental values of y ; the variance of a value of \underline{y} taken from the graph is given by ¹⁰³

$$\delta_y^2 = \delta_y^2 + X \delta_\alpha^2 \quad 150$$

Where δ_α^2 is the variance of the regression coefficient, α , δ_y^2 is the variance of the mean value of \underline{y} , and X the distance, in units of \underline{x} , from the mean of \underline{x} , \bar{x} , to the value of \underline{x} corresponding to \underline{y} .

δ_α^2 is given by: ¹⁰³

$$\delta_\alpha^2 = \delta_y^2 / \sum (x - \bar{x})^2 \quad 151$$

After substituting 151 in 150

$$\delta_y^2 = \delta_y^2 (1 + X/\sum (x - \bar{x})^2) \quad 152$$

For straight line plots of $1/S$ versus $1/K$, to determine the intercept at $1/S = 0$, $1/K_c$, (151) becomes

$$\delta_{(1/K_c)}^2 = \delta_{(1/K)}^2 \left[1 + (\bar{1/S}) / \sum (1/S - \bar{1/S})^2 \right] \quad 153$$

Therefore substituting equation 149 in equation 153 gives

$$\delta_{(1/K_c)}^2 = (\bar{c}^2/4) (1/K)^2 \left[1 + (\bar{1/S}) / \sum (1/S - \bar{1/S})^2 \right] \quad 154$$

Since the mean value, $\overline{1/K}$, lies on the regression line,

$$\overline{1/K} = (1/b) (\overline{1/S}) + 1/K_c$$

$$\int^2_{(1/K_c)} = \bar{c}^2/4 \left[(1/b) (\overline{1/S}) + 1/K_c \right]^2 \left[1 + \overline{1/S} / \sum (1/S - \overline{1/S})^2 \right]$$

(equation 155)

Hence, the 95% confidence limits $\pm d$, as a fraction of $1/K_c$, are given by

$$d = \bar{c} \left[1 + (1/b) (\overline{1/S}) / (1/K_c) \right] \left[1 + \overline{1/S} / \sum (1/S - \overline{1/S})^2 \right]^{1/2}$$

(equation 156)

The values of $\overline{1/S}$ used in kinetic determinations were approximately 1.18, 0.77, 0.59, 0.46.

Substituting these values in equation 156 gives

$$d = 1.80 \bar{c} \left[1 + 0.75 (1/b) / (1/K_c) \right] \quad 157$$

The value of the fractional change E in the value of 'b' (equation 144) was found to be between 0.15 and 0.05 for the kinetic runs and this gives a maximum fractional correction of

$$E^1 = 0.090 (1/b) / (1/K_c) \quad 158$$

The values of \bar{c} in equation 157 were given as 0.10 for copper and cobalt and 0.06 for nickel (page 89).

Hence, equation 157 becomes

$$d = 0.18 \left[1 + 0.75 (1/b) / (1/K_c) \right] \quad \text{for copper and cobalt} \quad 159$$

$$\text{and } d = 0.11 \left[1 + 0.75 (1/b) / (1/K_c) \right] \quad \text{for nickel} \quad 160$$

Examination of equations 158-160 shows that the fractional correction is always less than the limits of accuracy of the measurement of $1/K_c$, therefore there is little point in applying the correction, E^1 .

The accuracy of determination of $1/b$ can also be evaluated in a similar manner.

For a regression, $y = \alpha x + \beta$, if δ_y^2 is the residual variance of y , then $\delta_y^2 / \sum (x - \bar{x})^2$ is the residual variance of α .

For the equation, $1/K = (1/b) (1/S) + 1/K_c$, the residual variance of $1/b$ is given by

$$S_{(1/b)}^2 = \delta_{(1/k)}^2 / \sum [(1/s - \bar{1/s})^2] \quad 161$$

Substituting equation 14.9 in equation 161 gives

$$S_{(1/b)}^2 = (\bar{c}^2/4) (1/k)^2 / \sum [(1/s - \bar{1/s})^2] \quad 162$$

Since the regression passes through the mean, equation 162 can be written

$$S_{(1/b)}^2 = \bar{c}^2/4 \left[(1/b) (\bar{1/s}) + (1/k_c) \right]^2 / \sum (1/s - \bar{1/s})^2 \quad \text{(equation 162a)}$$

Hence, the 95% confidence limits, d' , for the accuracy of $1/b$ are given by

$$d' = \bar{c} \left[1/s + (1/k_c)/(1/b) \right] / \left(\sum (1/s - \bar{1/s})^2 \right)^{1/2} \quad 163$$

Substituting values of $1/s$ given on page 95 gives

$$d' = 1.35 \bar{c} \left[1 + 1.33 (1/k_c)/(1/b) \right] \quad 164$$

For copper and cobalt that gives

$$d' = 0.135 \left[1 + 1.33 (1/k_c)/(1/b) \right] \quad 165$$

and for nickel

$$d' = 0.081 \left[1 + 1.33 (1/k_c)/(1/b) \right] \quad 165a.$$

Summarising these formulae for accuracy of determination, expressed as percentages.

Accuracy of $1/k_c$

(a) Copper and Cobalt

$$d = 18 \left[1 + 0.75 (1/b)/(1/k_c) \right] \% \quad 166$$

(b) Nickel

$$d = 11 \left[1 + 0.75 (1/b)/(1/k_c) \right] \% \quad 166a$$

Accuracy of $1/b$

(a) Copper and Cobalt

$$d' = 13.5 \left[1 + 1.33 (1/k_c)/(1/b) \right] \% \quad 167$$

(b) Nickel

$$d' = 8.1 \left[1 + 1.33 (1/k_c)/(1/b) \right] \% \quad 167a.$$

Statistical Significance

The statistical significance of the values of $1/K_C$ and $1/b$ can be tested by using Students 't' test.

The value of 't' for some experimental value x , with standard deviation δx , is given by

$$t = x/\delta x$$

168.

A regression from four experimental points has two degrees of freedom and the significance at various levels of 't' is given below:

Significance level	0.1	0.05	0.02	0.01	0.001
't'	2.92	4.30	6.97	9.93	31.6

The value of 't' is related to the percentage errors (\underline{d} and \underline{d}') of $1/K_C$ and $1/b$ respectively by the equation

$$\begin{aligned} 't' &= 200/\underline{d} \quad \text{for } 1/K_C \\ \text{and } 't' &= 200/\underline{d}' \quad \text{for } 1/b \end{aligned}$$

N.B. Examination of equation 144 (page 91) shows that it is possible for the apparent value of $1/K'_C$ to be negative, i.e.

$$E (1/b) > (1/K_C) \left[S_2 (E + 1) - S_1 \right]$$

putting $S_2 = 2.15$, $S_1 = 0.83$ and $E = 0.10$

$$\text{gives } (1/b) > 15(1/K_C).$$

In these circumstances, the value of 't' for $1/K_C$ would be less than 1.0 for copper and cobalt, and less than 1.6 for nickel, i.e. not significant at the 10% level. Hence, for any graph of $1/K$ versus $1/S$ which shows an apparently negative value of $1/K_C$, it can be assumed that the result is not significant.

3.2.3(ii) Experimental Results

Complete tables of values of all measured concentrations are found in Appendix III.

- (a) For each metal a single initial run was carried out at constant stirring speed, to check that the rate of reaction is described by a simple first order law.

The mass transfer coefficient was calculated from the slope of a plot of $\log C_s$ against time, t . Experimental conditions were chosen, such that \bar{m} was large and $\log(C_s - C_w/\bar{m})$ was approximately $\log C_s$.

The results of the runs are shown below in Table XVII.

TABLE XVII

The conditions under which these runs were conducted were as follows:-

D.E.H.P. concentration: 0.05M (copper), 0.1M (nickel, 0.1M (cobalt).
 pH 2.75 (copper), 2.70 (nickel), 2.65 (cobalt).
 Temperature 20.5°C.
 Stirring Speed 77 r.p.m.
 Interfacial Area 62.6 cm².

Time Min.	Copper			Nickel			Cobalt		
	C_w $\times 10^3 M$	C_s $\times 10^3 M$	$\log C_s$	C_w $\times 10^3 M$	C_s $\times 10^3 M$	$\log C_s$	C_w $\times 10^3 M$	C_s $\times 10^3 M$	$\log C_s$
0	0.08	8.85	-2.053	0.23	6.21	-2.207	0.09	6.63	-2.178
15	0.43	8.50	-2.071	0.67	5.77	-2.239	0.52	6.20	-2.208
30	0.70	8.23	-2.085	1.14	5.30	-2.276	1.05	5.68	-2.245
45	1.11	7.82	-2.107	1.47	4.96	-2.305	1.42	5.30	-2.276
60	1.47	7.46	-2.127	1.76	4.68	-2.330	1.74	4.98	-2.303
75	1.86	7.07	-2.150	2.02	4.42	-2.355	2.04	4.68	-2.330
90	2.22	6.71	-2.173	2.26	4.18	-2.380	2.26	4.46	-2.350

Graphs of $\log C_s$ against time are shown in Figure XIV.

From these the mass transfer coefficients, K , were calculated using the equation:

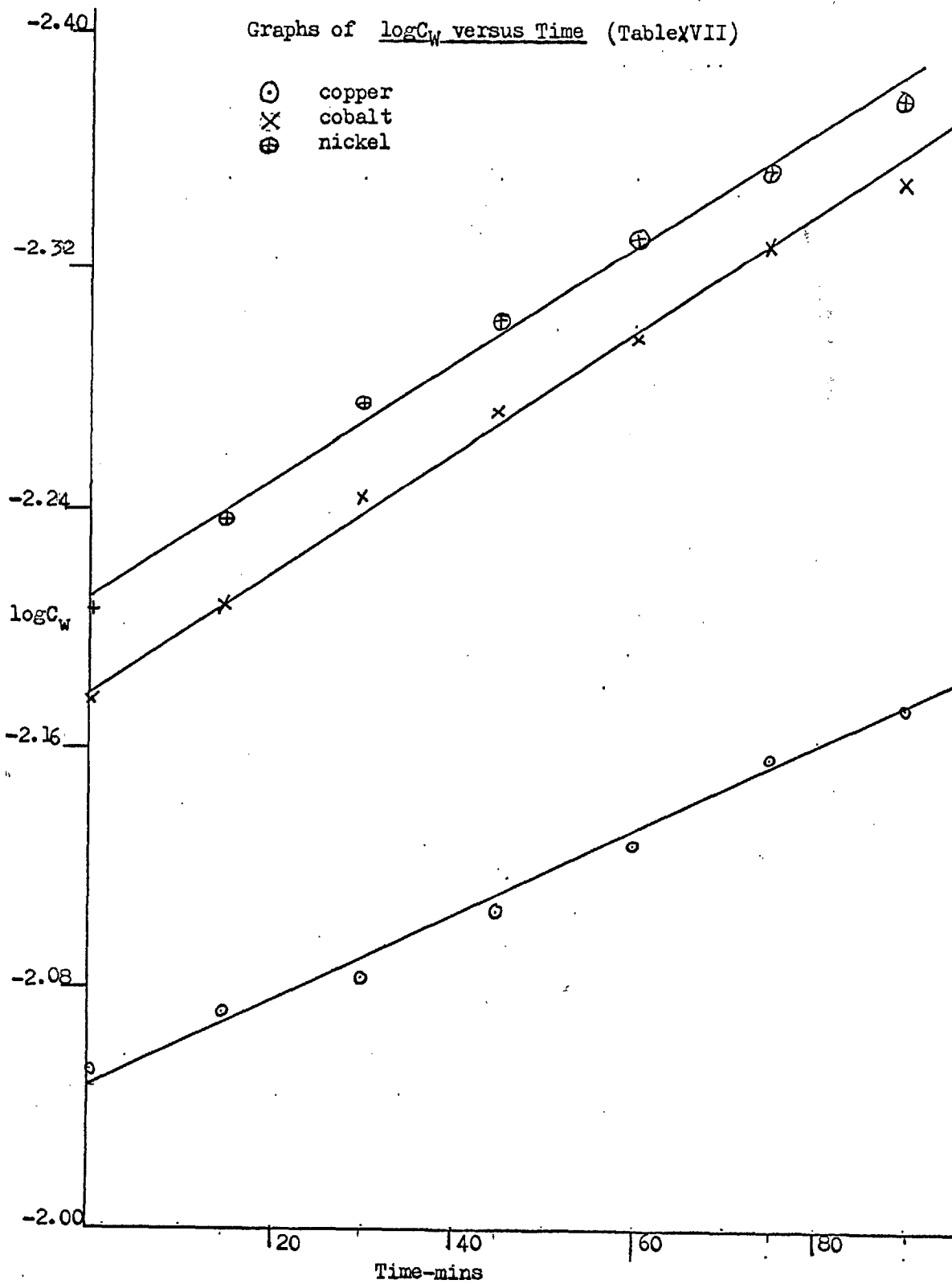
$$K = (V_w/A) \cdot 0.384 \Delta \log C_s / \Delta t$$

169.

The values of K , together with their standard deviations, δ_K , and percentage errors, are shown in Table XVIII.

TABLE XVIII.

Metal	K cm/sec.	δ_K	% Error
Copper	2.09×10^{-4}	0.069×10^{-4}	3.3
Nickel	3.02×10^{-4}	0.106×10^{-4}	3.5
Cobalt	3.06×10^{-4}	0.112×10^{-4}	3.7



These results, together with the other results to follow, will be discussed later (pages 151 -157).

All further runs were carried out with step-wise increases in stirring speed. Five stirring speeds were used, but the reciprocal of the value of the lowest stirring speed was more than twice that of the next higher value. It was therefore omitted from the graphs of $1/K$ versus $1/S$ to prevent it unduly weighting the values of the slope and intercept. Also, the approximation of equation 142 to equation 143 (page 89) does not hold at low stirring speeds.

The variables examined in these kinetic runs were:- organic phase metal concentration, D.E.H.P. concentration, pH, temperature and the effect of the presence of capryl alcohol. The experimental conditions used and the results obtained are as follows:-

(In all the runs the interfacial area was 62.6 cm^2 .)

TABLE XIX. The kinetics of the extraction of copper at 20.5°C as a function of organic metal concentration, with pH 2.50, and D.E.H.P. concentration 0.2 mole/litre.

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/ sec.	$C_s \times 10^3$ mole/litre	$C_w \times 10^3$ mole/litre	m	$C_s - C_w / m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
(a) Ex No. 49 $C_s^0 = 8.81 \times 10^{-3}$ mole/litre						
0.45	1.80	8.68	0.10	1.00	8.58	0.87
0.83	2.57	8.47	0.38	1.05	8.11	1.32
1.23	3.57	8.09	0.76	1.07	7.38	2.01
1.63	4.23	7.60	1.20	1.12	6.53	2.69
2.03	4.02	7.15	1.70	1.16	5.69	2.93
(b) Ex No. 50 $C_s^0 = 17.41 \times 10^{-3}$ mole/litre						
0.45	2.74	16.64	0.76	1.01	15.93	0.72
0.84	4.90	17.12	0.29	1.03	16.84	1.21
1.23	5.87	16.04	1.34	1.12	14.84	1.64
1.63	7.47	15.21	2.15	1.18	13.39	2.32
2.01	7.17	14.28	3.02	1.26	11.88	2.52
(c) Ex No. 51 $C_s^0 = 12.64 \times 10^{-3}$ mole/litre						
0.45	2.19	12.45	0.19	1.01	12.26	0.74
0.84	3.17	12.10	0.53	1.06	11.60	1.14
1.23	4.83	11.67	0.95	1.09	10.80	1.86
1.63	4.33	11.09	1.51	1.14	9.76	1.85
2.03	4.16	10.53	2.04	1.17	8.78	1.97
(d) Ex No. 52 $C_s^0 = 3.88 \times 10^{-3}$ mole/litre						
0.45	0.80	3.81	0.07	1.00	3.74	0.89
0.84	1.09	3.70	0.18	1.01	3.52	1.29
1.23	1.56	3.53	0.34	1.03	3.20	2.03
1.63	1.57	3.33	0.53	1.06	2.83	2.31
2.03	1.67	3.14	0.72	1.07	2.47	2.81

TABLE XX. The kinetics of the extraction of cobalt at 20.5°C as a function of organic metal concentration, with pH 2.90 and D.E.H.P. concentration 0.1 mole/litre.

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/ sec.	$C_s \times 10^3$ mole/litre	$C_v \times 10^3$ mole/litre	m	$C_s - C_v / m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
Ex No. 79		$C_s^0 = 14.15 \times 10^{-3}$ mole/litre				
0.43	1.40	13.96	0.19	6.5	13.93	0.42
0.87	3.90	13.55	0.59	6.8	13.46	1.20
1.30	5.77	13.06	1.07	7.2	12.91	1.86
1.73	7.66	12.18	1.92	7.8	11.93	2.67
2.17	7.52	11.18	2.86	8.3	10.83	2.88
Ex No. 80		$C_s^0 = 9.40 \times 10^{-3}$ mole/litre				
0.44	1.25	9.30	0.10	6.3	9.29	0.56
0.84	3.02	9.02	0.38	6.6	8.96	1.40
1.27	3.81	8.59	0.79	6.9	8.48	1.87
1.73	5.48	8.02	1.35	7.4	7.84	2.91
2.17	5.73	7.37	1.96	7.8	7.12	3.34
Ex No. 76		$C_s^0 = 6.64 \times 10^{-3}$ mole/litre				
0.52	1.19	6.48	0.16	6.4	6.45	0.78
0.87	2.99	6.27	0.37	6.6	6.22	2.00
1.30	3.86	5.83	0.80	6.9	5.72	2.80
1.73	4.40	5.27	1.33	7.4	5.09	3.60
2.17	3.96	4.75	1.83	7.7	4.51	3.64
Ex No. 81		$C_s^0 = 3.54 \times 10^{-3}$ mole/litre				
0.44	0.81	3.46	0.08	6.3	3.45	0.98
0.86	1.33	3.35	0.19	6.5	3.32	1.67
1.30	2.23	3.11	0.43	6.6	3.04	3.05
1.73	2.32	2.82	0.70	6.9	2.72	3.54
2.17	2.14	2.56	0.95	7.2	2.43	3.67

TABLE XXI. The kinetics of the extraction of nickel at 20.5°C as a function of organic metal concentration, with pH 2.90 and D.E.H.P. concentration 0.2 mole/litre.

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/ sec.	$C_s \times 10^3$ mole/litre	$C_w \times 10^3$ mole/litre	m	$C_s - C_w/m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
Ex No. 103 $C_s^0 = 12.36 \times 10^{-3}$ mole/litre						
0.57	4.00	11.77	0.59	5.3	11.66	1.43
0.87	3.69	11.35	1.00	5.6	11.11	1.38
1.28	4.63	10.83	1.50	5.8	10.59	1.83
1.72	6.93	10.10	2.20	6.2	9.75	2.96
2.15	7.22	9.22	3.04	6.4	8.75	3.43
Ex No. 104 $C_s^0 = 10.40 \times 10^{-3}$ mole/litre						
0.58	3.47	10.08	0.32	5.0	10.02	1.44
0.87	3.82	9.64	0.75	5.4	9.50	1.68
1.30	5.26	9.07	1.30	5.7	8.84	2.46
1.72	6.28	8.33	2.01	6.1	8.00	3.27
2.15	6.64	7.49	2.80	6.3	7.05	3.92
Ex no. 105 $C_s^0 = 4.81 \times 10^{-3}$ mole/litre						
0.58	1.11	4.72	0.09	4.8	4.70	0.98
0.87	2.02	4.52	0.29	5.0	4.45	1.89
1.30	2.60	4.23	0.57	5.3	4.12	2.63
1.72	3.08	3.88	0.90	5.5	3.72	3.45
2.15	2.95	3.50	1.27	5.7	3.28	3.74

TABLE XXII. The kinetics of the extraction of copper at 20.5°C as a function of D.E.H.P. concentration, with pH 2.50.

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/sec.	$C_s \times 10^3$ mole/litre	$C_w \times 10^3$ mole/litre	m	$C_s - C_w/m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
Ex No. 53	Conc. of D.E.H.P. = 0.4 mole/litre. $C_s^0 = 7.35 \times 10^{-3}$ mole/litre					
0.45	0.97	7.25	0.10	0.18	6.69	0.58
0.85	1.56	7.10	0.25	0.19	5.79	1.12
1.25	2.07	6.85	0.49	0.19	4.27	2.02
1.63	2.24	6.64	0.73	0.20	2.99	3.12
2.03	2.02	6.35	0.97	0.22	2.00	4.20
Ex No. 49	Conc. of D.E.H.P. = 0.2 mole/litre. $C_s^0 = 8.81 \times 10^{-3}$ mole/litre					
0.45	1.70	8.78	0.101	1.00	8.68	0.82
0.83	2.57	8.47	0.383	1.05	8.11	1.32
1.23	3.57	8.09	0.760	1.03	7.38	2.01
1.63	4.23	7.60	1.20	1.12	6.53	2.69
2.03	4.02	7.15	1.70	1.16	5.69	2.93
Ex No. 54	Conc. of D.E.H.P. = 0.1 mole/litre. $C_s^0 = 7.32 \times 10^{-3}$ mole/litre					
0.45	3.18	7.05	0.27	5.9	7.00	1.88
0.85	4.14	6.55	0.77	6.2	6.43	2.68
1.23	5.17	6.01	1.29	6.5	5.81	3.70
1.63	4.75	5.36	1.91	6.8	5.08	3.89
2.03	4.22	4.82	2.41	6.9	4.47	3.92
Ex No. 55	Conc. of D.E.H.P. = 0.05 mole/litre. $C_s^0 = 7.16 \times 10^{-3}$ mole/litre					
0.47	4.62	6.74	0.42	34	6.73	2.86
0.87	4.88	6.12	1.03	35	6.09	3.33
1.23	4.39	5.60	1.53	37	5.56	3.28
1.63	4.25	5.04	2.06	39	4.99	3.57
2.05	3.80	4.50	2.57	40	4.44	3.56
Ex No. 56	Conc. of D.E.H.P. = 0.025 mole/litre. $C_s^0 = 6.99 \times 10^{-3}$ mole/litre					
0.47	4.92	6.57	0.42	190	6.57	3.12
0.85	5.77	5.92	1.06	200	5.91	4.05
1.23	5.61	5.33	1.63	210	4.32	4.39
1.63	5.14	4.58	2.35	220	4.57	4.68
2.05	4.74	3.97	2.92	230	3.96	4.97

TABLE XXIII. The kinetics of the extraction of cobalt at 20.5°C as a function of D.E.H.P. concentration, with pH 2.90.

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/sec.	$C_S \times 10^3$ mole/litre	$C_W \times 10^3$ mole/litre	n	$C_S - C_W/m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
Ex No.82. Conc. of D.E.H.P. = 0.4 mole/litre. $C_S^0 = 6.64 \times 10^{-3}$ mole/litre						
0.48	0.39	6.59	0.05	0.31	6.43	0.25
0.87	1.34	6.49	0.15	0.32	6.42	0.87
1.30	1.52	6.31	0.32	0.32	5.31	1.19
1.75	2.08	6.05	0.57	0.33	4.33	2.00
2.17	2.30	5.79	0.82	0.34	3.39	2.82
Ex No.83. Conc. of D.E.H.P. = 0.2 mole/litre. $C_S^0 = 6.44 \times 10^{-3}$ mole/litre						
0.47	0.74	6.39	0.05	1.38	6.35	0.49
0.87	1.79	6.23	0.21	1.41	6.08	1.22
1.30	2.81	6.00	0.43	1.44	5.70	2.05
1.77	3.75	5.52	0.89	1.51	4.93	3.16
2.17	4.39	4.99	1.40	1.62	4.13	4.42
Ex No.76. Conc. of D.E.H.P. = 0.1 mole/litre. $C_S^0 = 6.64 \times 10^{-3}$ mole/litre						
0.52	1.19	6.48	0.16	6.4	6.45	0.78
0.87	2.99	6.27	0.37	6.6	6.22	2.00
1.30	3.86	5.83	0.80	6.9	5.72	2.80
1.73	4.40	5.27	1.33	7.4	5.09	3.60
2.17	3.96	4.75	1.83	7.7	4.51	3.64
Ex No.84. Conc. of D.E.H.P. = 0.05 mole/litre. $C_S^0 = 4.48 \times 10^{-3}$ mole/litre						
0.45	0.81	4.40	0.08	27	4.40	0.77
0.85	2.65	4.18	0.29	28	4.17	2.64
1.30	3.83	3.78	0.68	30	3.76	4.24
1.77	3.80	3.30	1.15	31	3.26	4.85
2.17	3.59	2.84	1.59	32	2.79	5.35

TABLE XXIV. The kinetics of the extraction of nickel at 20.5°C as a function of D.E.H.P. concentration, with pH 2.90.

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/ sec.	$C_s \times 10^3$ mole/litre	$C_w \times 10^3$ mole/litre	m	$C_s - C_w / m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
Ex No.106. Conc. of D.E.H.P. = 0.4 mole/litre. $C_s^0 = 6.64 \times 10^{-3}$ mole/litre						
0.85	1.39	6.49	0.15	0.71	6.28	0.92
1.30	1.91	6.38	0.36	0.74	5.89	1.35
1.73	2.29	6.01	0.61	0.74	5.19	1.84
2.17	2.32	5.73	0.88	0.78	4.61	2.09
Ex No.105. Conc. of D.E.H.P. = 0.2 mole/litre. $C_s^0 = 4.81 \times 10^{-3}$ mole/litre						
0.58	1.11	4.72	0.09	4.8	4.70	0.98
0.87	2.02	4.52	0.29	5.0	4.47	1.89
1.30	2.60	4.23	0.57	5.3	4.12	2.63
1.72	3.08	3.88	0.90	5.5	3.72	3.45
2.15	2.95	3.50	1.27	5.7	3.28	3.74
Ex No.99. Conc. of D.E.H.P. = 0.1 mole/litre. $C_s^0 = 6.44 \times 10^{-3}$ mole/litre						
0.58	2.67	6.17	0.27	23	6.16	1.80
0.87	3.64	5.76	0.66	24	5.73	2.65
1.28	4.76	5.26	1.15	25	5.22	3.80
1.72	4.40	4.68	1.72	26	4.61	3.98
2.15	4.38	4.14	2.22	28	4.06	4.43
Ex No.107. Conc. of D.E.H.P. = 0.05 mole/litre. $C_s^0 = 3.87 \times 10^{-3}$ mole/litre						
0.82	2.83	3.59	0.28	130	3.59	3.28
1.30	3.33	3.17	0.69	140	3.16	4.38
1.73	2.81	2.76	1.09	140	2.75	4.25
2.15	2.90	2.44	1.38	150	2.43	4.96

TABLE XXV. The kinetics of the extraction of copper at 20.5°C as a function of pH, with initial organic metal concentration 8.90×10^{-3} mole/litre and D.E.H.P. concentration 0.05 mole/litre.

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/sec.	$C_s \times 10^3$ mole/litre	$C_w \times 10^3$ mole/litre	m	$C_s - C_w/m$ mole/litre	$K \times 10^4$ cm/sec.
Ex No. 57		pH 3.00				
0.45	1.74	8.77	0.13	3.9	8.74	0.83
0.85	2.14	8.53	0.36	4.0	8.44	1.05
1.27	2.79	8.20	0.68	4.2	8.04	1.44
1.65	3.20	7.87	1.01	4.4	7.64	1.74
2.05	3.58	7.46	1.41	4.5	7.15	2.08
Ex No. 58		pH 2.70				
0.43	2.18	8.74	0.16	13.5	8.73	1.04
0.83	3.49	8.39	0.50	14.0	8.36	1.73
1.25	4.78	7.93	0.95	15.0	7.87	2.53
1.65	5.34	7.21	1.65	16.0	7.11	3.12
2.05	5.18	6.59	2.23	16.5	6.46	3.34
Ex No. 59		pH 2.40				
0.43	6.48	8.40	0.50	52	8.39	3.21
0.82	6.87	7.51	1.38	56	7.48	3.82
1.25	7.44	6.70	2.16	59	6.66	4.66
1.65	6.62	5.78	3.03	62	5.73	4.80
2.05	6.18	4.97	3.79	64	4.91	5.22
Ex No. 60		pH 2.10				
0.43	9.37	8.19	0.71	200	8.19	4.77
0.82	8.75	7.05	1.83	210	7.04	5.16
1.23	7.72	5.98	2.86	220	5.97	5.39
1.65	6.15	5.13	3.67	230	5.11	5.02
2.07	5.33	4.38	4.36	240	4.36	5.08

TABLE XXVI. The kinetics of the extraction of cobalt at 20.5°C as a function of pH, with initial organic metal concentration 6.64×10^{-3} mole/litre and D.E.H.P. concentration 0.10 mole/litre.

Stirrer Speed rev/sec.	$R \times 10^4$ mole/litre/sec.	$C_s \times 10^3$ mole/litre	$C_w \times 10^3$ mole/litre	m	$C_s - C_w / m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
Ex No. 77		pH 3.20				
0.50	0.67	6.56	0.08	1.85	6.52	0.43
0.87	1.20	6.41	0.22	1.90	6.29	0.79
1.30	2.42	6.24	0.39	2.0	6.04	1.67
1.73	3.17	5.88	0.74	2.1	5.53	2.39
2.17	3.74	5.46	1.14	2.2	4.94	3.15
Ex No. 76		pH 2.90				
0.52	1.19	6.48	0.16	6.4	6.45	0.78
0.87	2.99	6.27	0.37	6.6	6.22	2.00
1.30	3.86	5.83	0.80	6.9	5.72	2.80
1.73	4.40	5.27	1.33	7.4	5.09	3.60
2.17	3.96	4.75	1.83	7.7	4.51	3.64
Ex No. 75		pH 2.60				
0.52	3.35	6.33	0.31	21.5	6.32	2.21
0.87	5.35	5.79	0.84	22.5	5.75	3.87
1.27	5.06	5.08	1.53	24	5.02	4.18
1.72	4.67	4.55	2.04	25	4.47	4.35
2.17	4.41	3.94	2.60	26	3.84	4.78
Ex No. 78		pH 2.30				
0.50	5.10	6.24	0.40	75	6.23	3.40
0.88	3.77	5.76	0.87	78	5.75	2.73
1.32	3.97	5.25	1.37	79	5.23	3.16
1.75	3.22	4.86	1.73	82	4.84	2.77
2.17	3.59	4.35	2.22	83	4.32	3.46

TABLE XXVII. The kinetics of the extraction of nickel at 20.5°C as a function of pH, with initial organic metal concentration 6.44×10^{-3} mole/litre and D.E.H.P. concentration 0.1 mole/litre.

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/ sec.	$C_S \times 10^3$ mole/litre	$C_W \times 10^3$ mole/litre	m	$C_S - C_W/m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
Ex No. 100		pH 3.20				
0.50	0.80	6.35	0.09	6.6	6.34	0.53
0.85	1.46	6.21	0.23	6.8	6.18	0.98
1.28	1.87	6.01	0.42	7.1	5.95	1.31
1.72	2.09	5.76	0.66	7.3	5.67	1.53
2.15	2.60	5.45	0.95	7.6	5.32	2.03
Ex No. 99		pH 2.90				
0.58	2.67	6.17	0.27	23	6.16	1.80
0.87	3.64	5.76	0.66	24	5.73	2.65
1.28	4.76	5.26	1.15	25	5.22	3.80
1.72	4.40	4.68	1.72	26	4.61	3.98
2.15	4.38	4.14	2.22	28	4.06	4.48
Ex No. 101		pH 2.60				
0.57	3.74	6.13	0.31	76	6.13	2.54
0.88	4.35	5.64	0.79	79	5.63	3.26
1.28	4.66	5.07	1.35	84	5.05	3.83
1.72	4.04	4.54	1.85	87	4.52	3.71
2.15	3.28	4.09	2.25	89	4.06	3.37
Ex No. 102		pH 2.30				
0.51	5.18	5.91	0.53	270	5.91	3.65
0.85	5.80	5.19	1.23	280	5.19	4.65
1.28	4.68	4.60	1.81	290	4.59	4.24
1.72	4.05	4.06	2.31	300	4.05	4.16
2.15	3.66	3.56	2.78	310	3.55	4.30

TABLE XXVIII. The kinetics of the extraction of copper as a function of temperature, with initial organic metal concentration 8.90×10^{-3} mole/litre, pH 2.60 and D.E.H.P. concentration 0.05 mole/litre.

Stirrer Speed rev./sec.	$R \times 10^7$ mole/litre/sec.	$C_s \times 10^3$ mole/litre	$C_w \times 10^3$ mole/litre	m	$C_s - C_w/m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
Ex No. 88		7°C.				
0.38	2.40	8.65	0.25	29	8.64	1.15
0.81	2.86	8.31	0.58	30	8.29	1.43
1.22	4.10	7.89	0.99	31	7.86	2.17
1.67	4.81	7.32	1.54	32	7.25	2.76
2.08	5.14	6.65	2.18	34	6.59	3.24
Ex No. 92		14°C.				
0.43	2.87	8.65	0.25	25	8.64	1.38
0.82	4.33	8.24	0.66	26	8.22	2.19
1.22	5.88	7.61	1.26	27	7.56	3.23
1.67	6.90	6.76	2.09	28	6.69	4.29
2.10	7.36	5.87	2.92	33	5.78	5.29
Ex No. 94		20.5°C.				
0.61	3.78	8.56	0.34	22	8.55	1.84
0.86	5.81	7.97	0.92	23	7.93	3.04
1.29	5.78	7.27	1.60	24	7.20	3.34
1.72	7.91	6.52	2.32	25	6.43	5.10
2.16	6.80	5.72	3.08	28	5.61	5.04
Ex No. 93		26.5°C.				
0.60	3.84	8.54	0.36	19	8.52	1.87
0.87	5.44	8.03	0.87	20	7.99	2.83
1.29	6.06	7.24	1.63	21	7.16	3.52
1.73	6.48	6.47	2.35	22	6.36	4.24
2.15	7.92	5.49	3.30	24	5.35	6.15

TABLE XXIX. The kinetics of the extraction of cobalt as a function of temperature, with initial organic metal concentration 6.64×10^{-3} mole/litre, pH 2.90 and D.E.H.P. concentration 0.1 mole/litre.

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/ sec.	$C_s \times 10^3$ mole/litre	$C_w \times 10^3$ mole/litre	m	$C_s - C_w/m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
Ex No. 87		7°C.				
0.43	0.68	6.58	0.06	8.5	6.57	0.43
0.82	1.36	6.49	0.17	8.6	6.47	0.87
1.23	2.46	6.25	0.39	8.9	6.21	1.65
1.65	2.87	5.86	0.75	9.3	5.78	2.07
2.08	3.26	5.51	1.10	9.6	5.40	2.51
Ex No. 91		14°C.				
0.44	0.76	6.58	0.06	7.3	6.57	0.48
0.82	1.62	6.43	0.21	7.5	6.40	1.05
1.22	2.13	6.17	0.46	7.7	6.11	1.45
1.67	3.38	5.83	0.79	8.0	5.73	2.45
2.10	4.95	5.38	1.22	8.6	5.24	3.92
Ex No. 76		20.5°C.				
0.52	1.19	6.48	0.16	6.4	6.45	0.78
0.87	2.99	6.27	0.37	6.6	6.22	2.00
1.30	3.86	5.83	0.80	6.9	5.72	2.80
1.73	4.40	5.27	1.33	7.4	5.09	3.60
2.17	3.96	4.75	1.83	7.7	4.59	3.64
Ex No. 86		26.5°C.				
0.47	0.95	6.55	0.09	5.4	6.53	0.60
0.87	2.50	6.34	0.30	5.7	6.29	1.65
1.31	4.21	5.95	0.68	5.9	5.83	3.00
1.73	4.57	5.42	1.19	6.3	5.23	3.63
2.17	4.37	4.83	1.75	6.6	4.56	3.90

TABLE XXX. The kinetics of the extraction of nickel as a function of temperature, with initial organic metal concentration 6.44×10^{-3} mole/litre, pH 2.90 and D.E.H.P. concentration 0.1 mole/litre.

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/ sec.	$C_s \times 10^3$ mole/litre	$C_w \times 10^3$ mole/litre	m	$C_s - C_w/m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
Ex No. 89		7°C.				
0.42	1.23	6.22	0.22	18	6.21	0.82
0.82	2.55	5.98	0.46	19	5.96	1.78
1.22	3.04	5.65	0.77	21	5.61	2.25
1.65	3.67	5.24	1.17	22	5.19	2.94
2.08	3.91	4.79	1.59	23	4.72	3.45
Ex No. 90		14°C.				
0.43	1.82	6.14	0.30	21	6.13	1.23
0.82	2.92	5.83	0.61	22	5.80	2.09
1.22	3.52	5.44	0.98	23	5.40	2.71
1.67	3.90	4.97	1.43	24	4.91	3.30
2.08	4.48	4.49	1.89	25	4.42	4.21
Ex No. 99		20.5°C.				
0.58	2.67	6.17	0.27	23	6.16	1.80
0.87	3.64	5.76	0.66	24	5.73	2.65
1.28	4.76	5.26	1.15	25	5.22	3.80
1.72	4.40	4.68	1.72	26	4.61	3.98
2.15	4.38	4.14	2.22	28	4.06	4.48
Ex No. 98		26.5°C.				
0.51	2.82	6.19	0.25	24	6.18	1.90
0.86	4.12	5.71	0.72	25	5.68	3.01
1.28	4.04	5.21	1.20	27	5.16	3.26
1.72	4.48	4.63	1.76	28	4.57	4.08
2.17	4.20	4.07	2.29	30	3.97	4.40

TABLE XXXI. The kinetics of the extraction of copper at 20.5°C in the presence of capryl alcohol, with initial organic metal concentration 8.02×10^{-3} mole/litre, pH 2.70 and D.E.H.P. concentration 0.1 mole/litre.

Ex No. 96

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/sec.	$C_S \times 10^3$ mole/litre	$C_W \times 10^3$ mole/litre	m	$C_S - C_W/m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
0.46	2.39	7.69	0.33	4.7	7.62	1.30
0.86	3.31	7.27	0.74	4.9	7.12	1.93
1.30	4.35	6.86	1.14	5.1	6.64	2.73
1.72	5.36	6.11	1.86	5.5	5.77	3.87
2.15	7.10	5.38	2.56	5.7	4.93	6.00

TABLE XXXII. The kinetics of the extraction of cobalt at 20.5°C in the presence of capryl alcohol, with initial organic metal concentration 7.32×10^{-3} mole/litre, pH 2.90 and D.E.H.P. concentration 0.1 mole/litre.

Ex No. 85

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/sec.	$C_S \times 10^3$ mole/litre	$C_W \times 10^3$ mole/litre	m	$C_S - C_W/m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
0.46	1.54	7.21	0.11	13.5	7.20	0.98
0.88	3.16	6.89	0.43	14.0	6.86	1.91
1.32	5.86	6.34	0.96	15.0	6.28	3.88
1.74	7.03	5.54	1.73	16.0	5.43	5.39
2.15	8.84	4.52	2.70	17.5	4.37	8.40

TABLE XXXIII. The kinetics of the extraction of nickel at 20.5°C in the presence of capryl alcohol, with initial organic metal concentration 4.81×10^{-3} mole/litre, pH 2.90 and D.E.H.P. concentration 0.1 mole/litre.

Ex No. 108

Stirrer Speed rev/sec.	$R \times 10^7$ mole/litre/sec.	$C_S \times 10^3$ mole/litre	$C_W \times 10^3$ mole/litre	m	$C_S - C_W/m \times 10^3$ mole/litre	$K \times 10^4$ cm/sec.
0.50	1.35	4.58	0.23	16.5	4.57	1.23
0.87	3.11	4.33	0.47	17.0	4.30	3.01
1.30	3.92	3.87	0.92	18.0	3.82	4.27
1.72	4.05	3.33	1.44	19.0	3.25	5.18
2.15	4.47	2.80	1.94	20.0	2.70	6.88

In all cases the capryl alcohol concentration was 0.5 mole/litre.

The data, in Tables XIX to XXI, for the kinetics of extraction as a function of organic metal concentration are shown graphically as $1/K$ versus $1/S$ in Figures XV to XVII. Values of $1/K_c$ and $1/b$ have been obtained from these graphs and are shown in Table XXXIV (a-c) together with their significance and degree of error. Theoretical values of $1/b$ have also been calculated, using equations 145-147 (page 91), and inserted in the table for comparison (the values of $1/K_w$ derived from equations 145-147 are the same as $1/b$ if values of individual species' mass transfer coefficients at one revolution per second are used).

The data in Tables XXII to XXIV for the kinetics of extraction as a function of D.E.H.P. concentration are shown graphically as $1/K$ versus $1/S$ in Figures XVIII to XX and values of $1/K_c$ and $1/b$ obtained from these graphs are shown in Table XXXV (a-c). Similar graphs of $1/K$ versus $1/S$ are shown in Figures XXI to XXIII for the kinetics of extraction as a function of pH, and in Figures XXIV to XXVI for the kinetics as a function of temperature; values of $1/K_c$ and $1/b$ obtained from these graphs are shown in Table XXXVI (a-c) and XXXVII (a-c) respectively for pH and temperature. Graphs of $1/K$ versus $1/S$ for the kinetics of extraction in the presence of capryl alcohol are shown in Figure XXVII, and the values of $1/K_c$ and $1/b$ obtained are in Table XXXVIII.

Discussion of these kinetic results and related graphs can be found later on pages 151 -155.

TABLE XXXIV.

Values of $1/K_c$ and $1/b$ for the kinetics of the extraction of copper, cobalt and nickel as a function of mean driving force.

Mean ($C_s - C_w/m$) $\times 10^3$ mole/litre	$1/K_c \times 10^{-4}$ sec/cm.	Significance	$1/b \times 10^{-4}$ cm ⁻¹	Significance	$1/b \times 10^{-4}$ cm ⁻¹ (calc.)
(a) Copper					
6.90	0.05(5) $\pm 160\%$	None	0.57 $\pm 15\%$	>0.01	0.80
14.36	0.09 $\pm 110\%$	"	0.61 $\pm 16\%$	>0.01	1.32
10.19	0.10 $\pm 110\%$	"	0.65(5) $\pm 16\%$	>0.01	1.01
3.00	0.08(5) $\pm 110\%$	"	0.54(5) $\pm 16\%$	>0.01	0.50(5)
(b) Cobalt					
12.14	0.02 $\pm 380\%$	None	0.68(5) $\pm 14\%$	>0.01	1.99
8.04	0.03 $\pm 280\%$	"	0.58 $\pm 14\%$	>0.01	1.36
5.37	0.10 $\pm 65\%$	0.1	0.35 $\pm 19\%$	>0.01	0.93
2.88	0.05 $\pm 130\%$	None	0.43 $\pm 16\%$	>0.01	0.58
(c) Nickel					
10.25	0.04(5) $\pm 120\%$	None	0.57 $\pm 9\%$	>0.01	1.67
8.20	0.03 $\pm 130\%$	"	0.48(5) $\pm 9\%$	>0.01	1.42
3.84	0.06 $\pm 67\%$	0.1	0.41 $\pm 10\%$	>0.01	0.71

TABLE XXXV. Values of $1/K_c$ and $1/b$ for the kinetics of the extraction of copper, cobalt and nickel as a function of D.E.H.P. concentration.

D.E.H.P. Conc. mole/litre	$1/K_c \times 10^{-4}$ sec/cm.	Significance	$1/b \times 10^{-4}$ cm ⁻¹	Significance	$1/b$ (calc.) $\times 10^{-4}$ cm ⁻¹
(a) Copper					
0.4	Negative	None	0.89 \pm 14%	>0.01	1.25
0.2	0.05(5) \pm 160%	"	0.57 \pm 16%	>0.01	0.80
0.1	0.16 \pm 32%	0.02	0.16(5) \pm 31%	0.02	0.48
0.05	0.24 \pm 21%	0.01	0.06 \pm 90%	<0.1	0.38
0.025	0.18 \pm 21%	0.01	0.05(5) \pm 75%	<0.1	0.32
(b) Cobalt					
0.4	Negative	None	1.15 \pm 14%	>0.01	1.59
0.2	Negative	"	0.83 \pm 14%	>0.01	1.13
0.1	0.10 \pm 65%	0.1	0.35 \pm 19%	>0.01	0.93
0.05	0.07 \pm 62%	0.1	0.23 \pm 19%	>0.01	0.58
(c) Nickel					
0.4	0.05 \pm 160%	None	0.88 \pm 9%	>0.01	1.20
0.2	0.06 \pm 67%	0.1	0.41 \pm 10%	>0.01	0.71
0.1	0.11 \pm 28%	0.02/0.01	0.22 \pm 13%	>0.01	0.77
0.05	0.13 \pm 20%	>0.1	0.14 \pm 18%	>0.01	0.40

TABLE XXXVI. Values of $1/K_c$ and $1/b$ for the kinetics of the extraction of copper, cobalt and nickel as a function of pH.

pH	$1/K_c \times 10^{-4}$ sec/cm.	Significance	$1/b \times 10^{-4}$ cm ⁻¹	Significance	$1/b(\text{calc})_1 \times 10^{-4}$ cm ⁻¹
(a) Copper					
3.0	0.16 \pm 74%	< 0.1	0.67 \pm 18%	> 0.01	1.74
2.7	0.10 \pm 70%	0.1	0.39 \pm 18%	> 0.01	0.80
2.4	0.15 \pm 25%	0.02/0.01	0.07(5) \pm 48%	0.05	0.34
2.1	0.18 \pm 11%	> 0.01	Not significant	None	0.22
(b) Cobalt					
3.2	Negative	None	1.10 \pm 11%	> 0.01	2.22
2.9	0.10 \pm 65%	0.1	0.35 \pm 19%	> 0.01	0.93
2.6	0.18 \pm 24%	0.02/0.01	0.07(5) \pm 57%	0.1/0.05	0.42
2.3	0.22 \pm 25%	0.02/0.01	0.12 \pm 47%	0.05	0.31
(c) Nickel					
3.2	0.15 \pm 56%	0.1/0.05	0.77 \pm 10%	> 0.01	1.84
2.9	0.11 \pm 28%	0.02/0.01	0.22 \pm 13%	> 0.01	0.77
2.6	0.22 \pm 11%	> 0.01	0.07(5) \pm 34%	0.02	0.37
2.3	0.21(5) \pm 11%	> 0.01	Not significant	None	0.24

TABLE XXXVII. Values of $1/K_c$ and $1/b$ for the kinetics of the extraction of copper, cobalt and nickel as a function of temperature.

Temp. °C	$1/K_c \times 10^{-4}$ sec/cm.	Significance	$1/b \times 10^{-4}$ cm ⁻¹	Significance
(a) Copper				
7	0.09 ± 87%	None	0.46 ± 17%	>0.01
14	0.03 ± 180%	"	0.35 ± 16%	>0.01
20.5	0.05 ± 96%	"	0.29 ± 17%	>0.01
26.5	0.06 ± 79%	"	0.28 ± 18%	>0.01
(b) Cobalt				
7	Not significant	None	1.02 ± 14%	>0.01
14	" "	"	0.94 ± 14%	>0.01
20.5	0.10 ± 65%	0.1	0.35 ± 19%	>0.01
26.5	0.01 ± 670%	None	0.50 ± 14%	>0.01
(c) Nickel				
7	0.14 ± 31%	0.05/0.02	0.35 ± 12%	>0.01
14	0.11 ± 34%	0.05/0.02	0.30 ± 12%	>0.01
20.5	0.11 ± 28%	0.02	0.22 ± 13%	>0.01
26.5	0.15 ± 20%	0.02/0.01	0.17 ± 18%	>0.01

TABLE XXXVIII. Values of $1/K_c$ and $1/b$ for the kinetics of the extraction of copper, cobalt and nickel in the presence of capryl alcohol. In the last two columns, values of $1/K_c$ in the absence of capryl alcohol are given for comparison.

Metal	$1/K_c \times 10^{-4}$ sec/cm.	Significance	$1/b \times 10^{-4}$ cm.	Significance	No capryl alcohol	
					$1/K_c \times 10^{-4}$ sec/cm.	Significance
Copper	Not significant	None	0.50 ± 14%	>0.01	0.10 ± 75%	0.1
Cobalt	"	"	0.54 ± 14%	>0.01	0.11 ± 65%	0.1
Nickel	0.01	"	0.29 ± 9%	>0.01	0.11 ± 28%	0.02/0.01

FIG XV

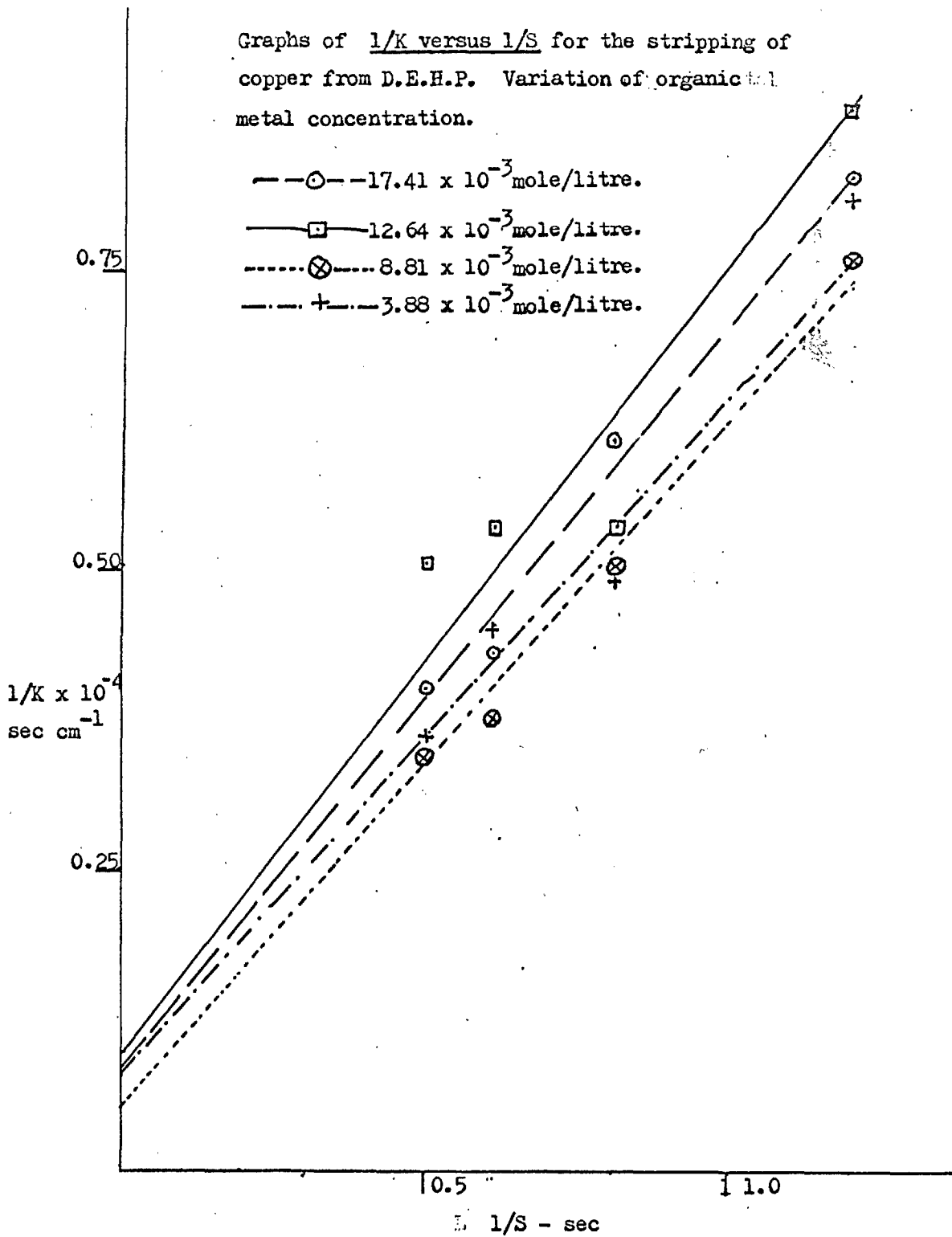


FIG XVI

Graphs of $1/K$ versus $1/S$ for the stripping of cobalt from D.E.H.P. Variation of organic metal concentration.

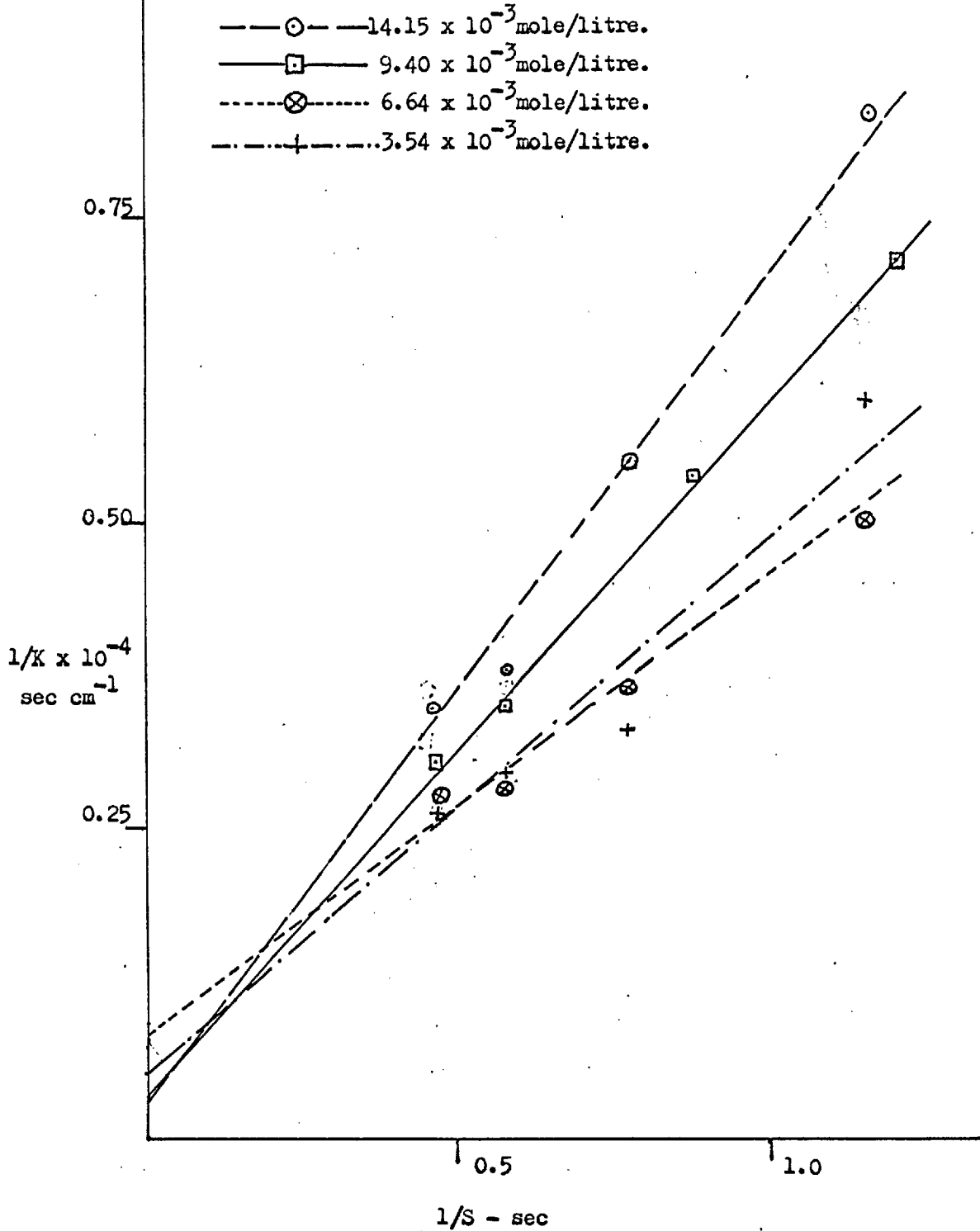


FIG XVII

Graphs of $1/K$ versus $1/S$ for the stripping of nickel from D.E.H.P. Variation of organic metal concentration.

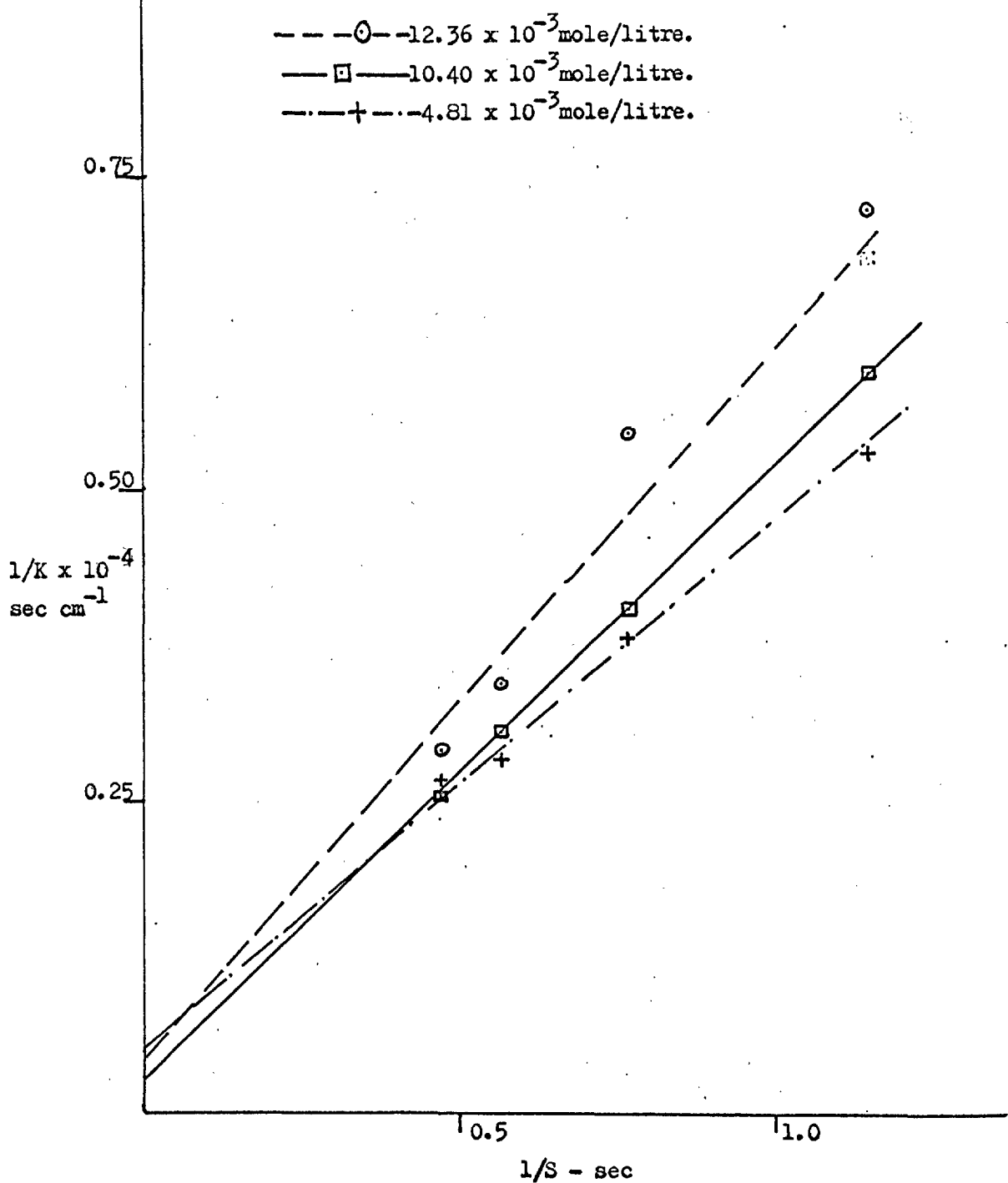


FIG XVIII

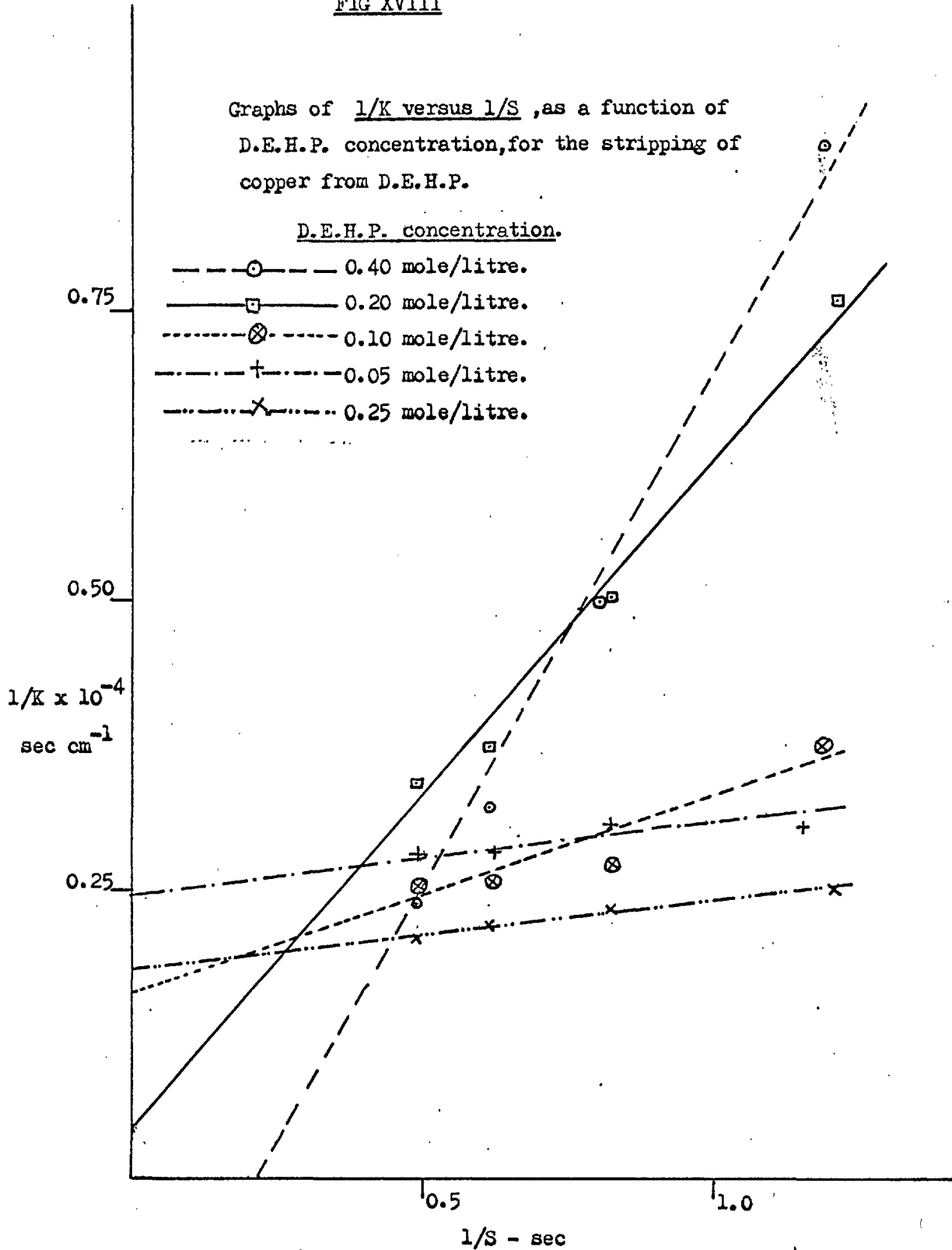


FIG XIX

Graphs of $1/K$ versus $1/S$, as a function of D.E.H.P. concentration, for the stripping of cobalt from D.E.H.P.

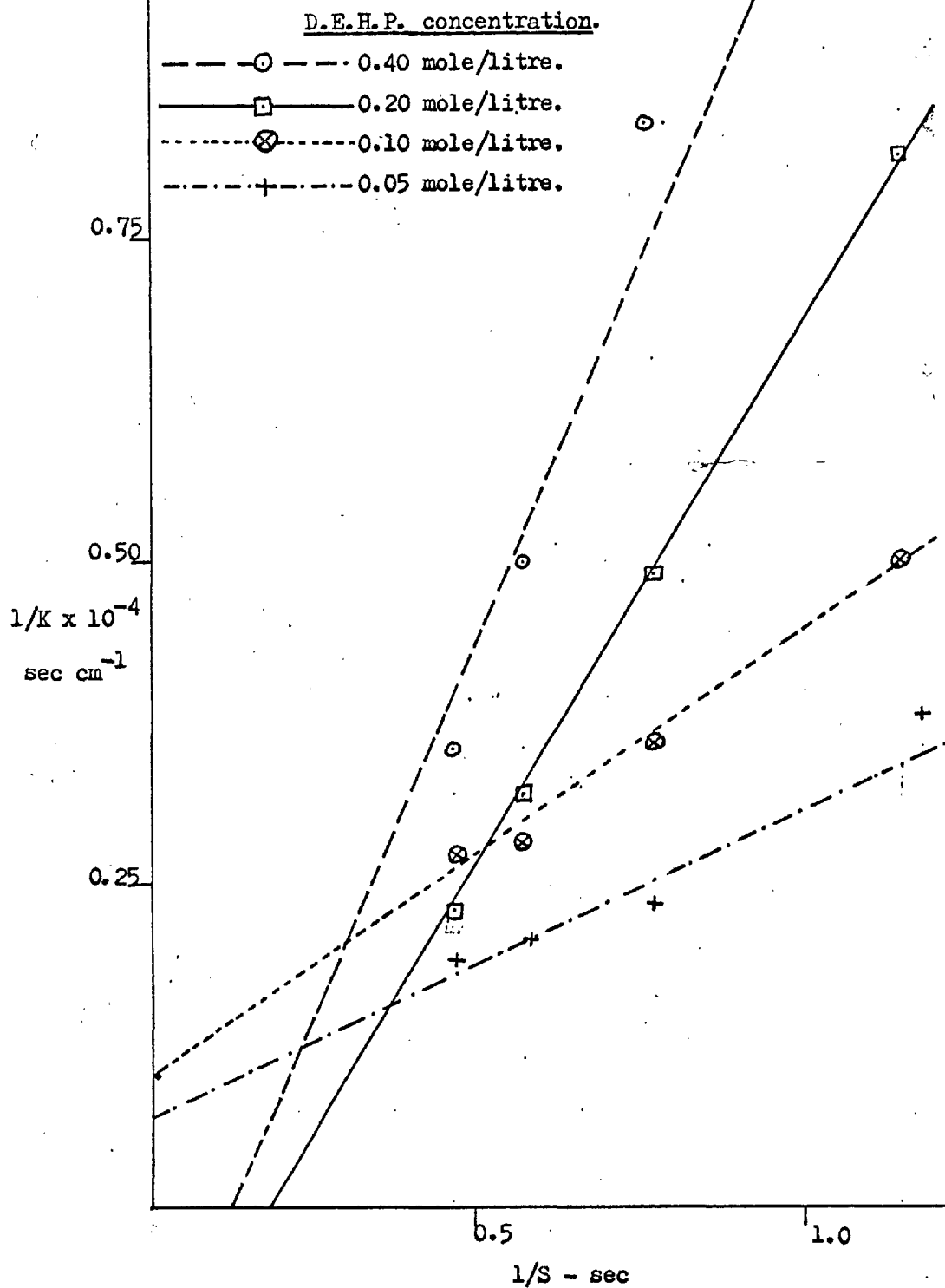


FIG XX

Graphs of $1/K$ versus $1/S$, as a function of D.E.H.P. concentration, for the stripping of nickel from D.E.H.P.

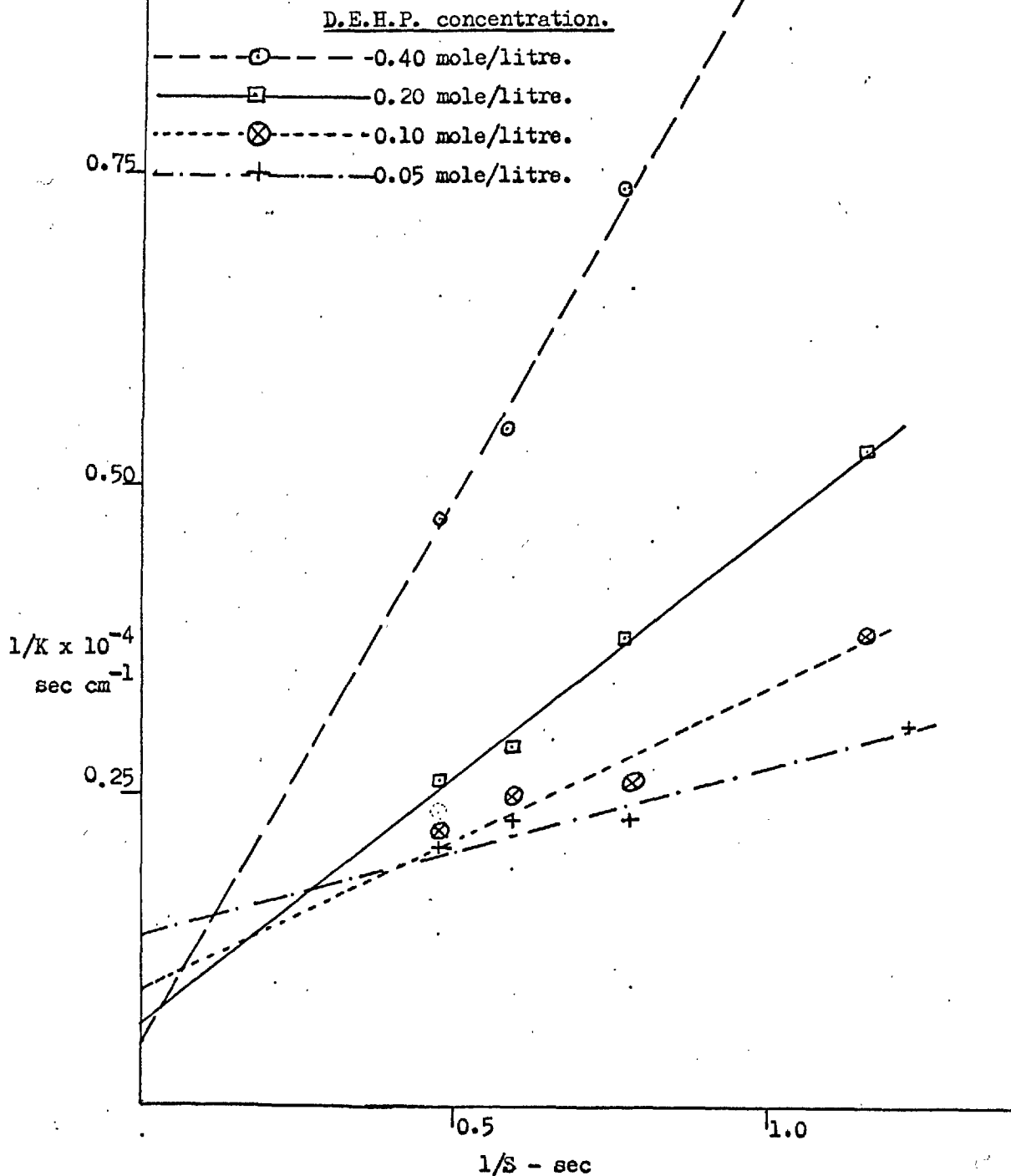


FIG XXI

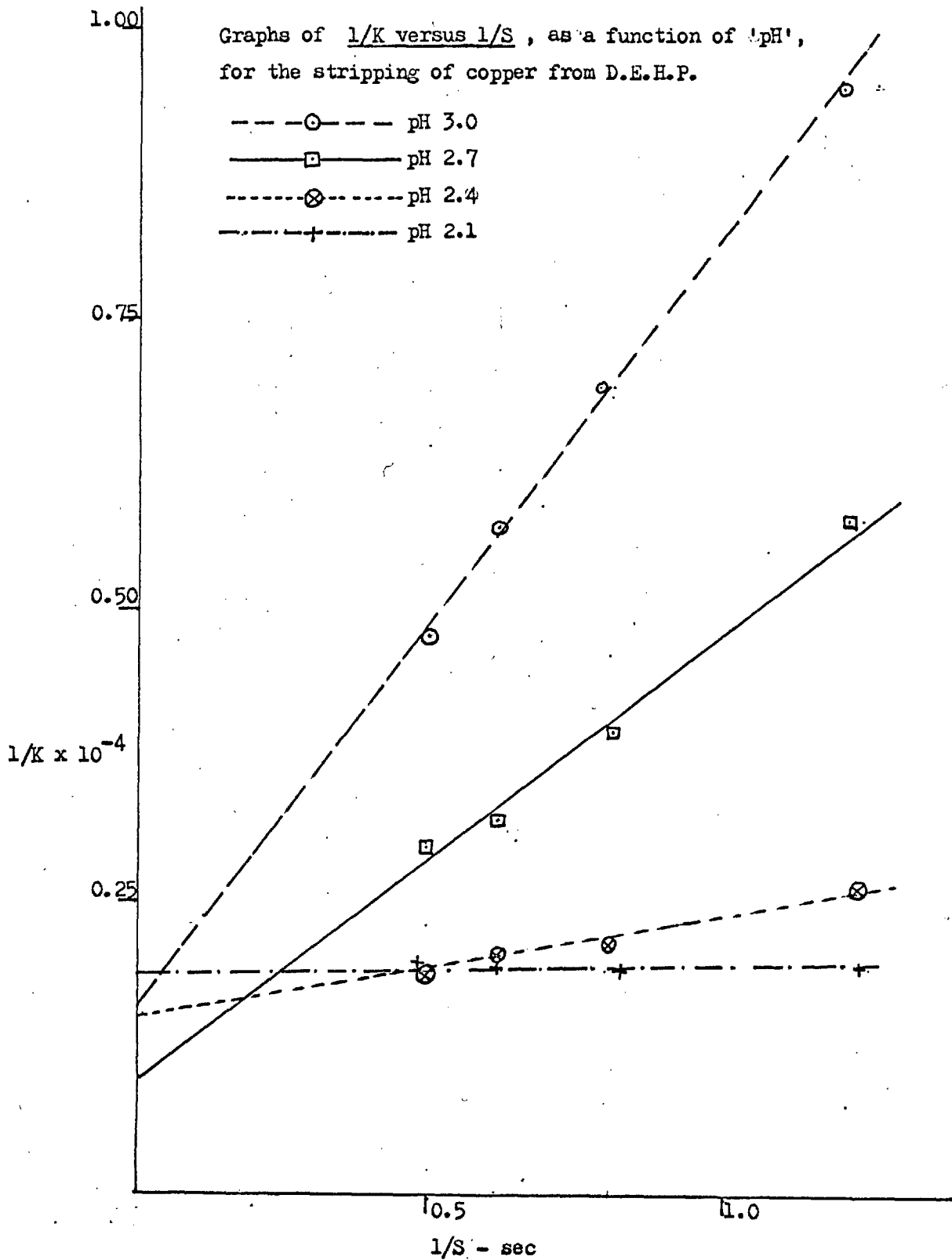


FIG XXII

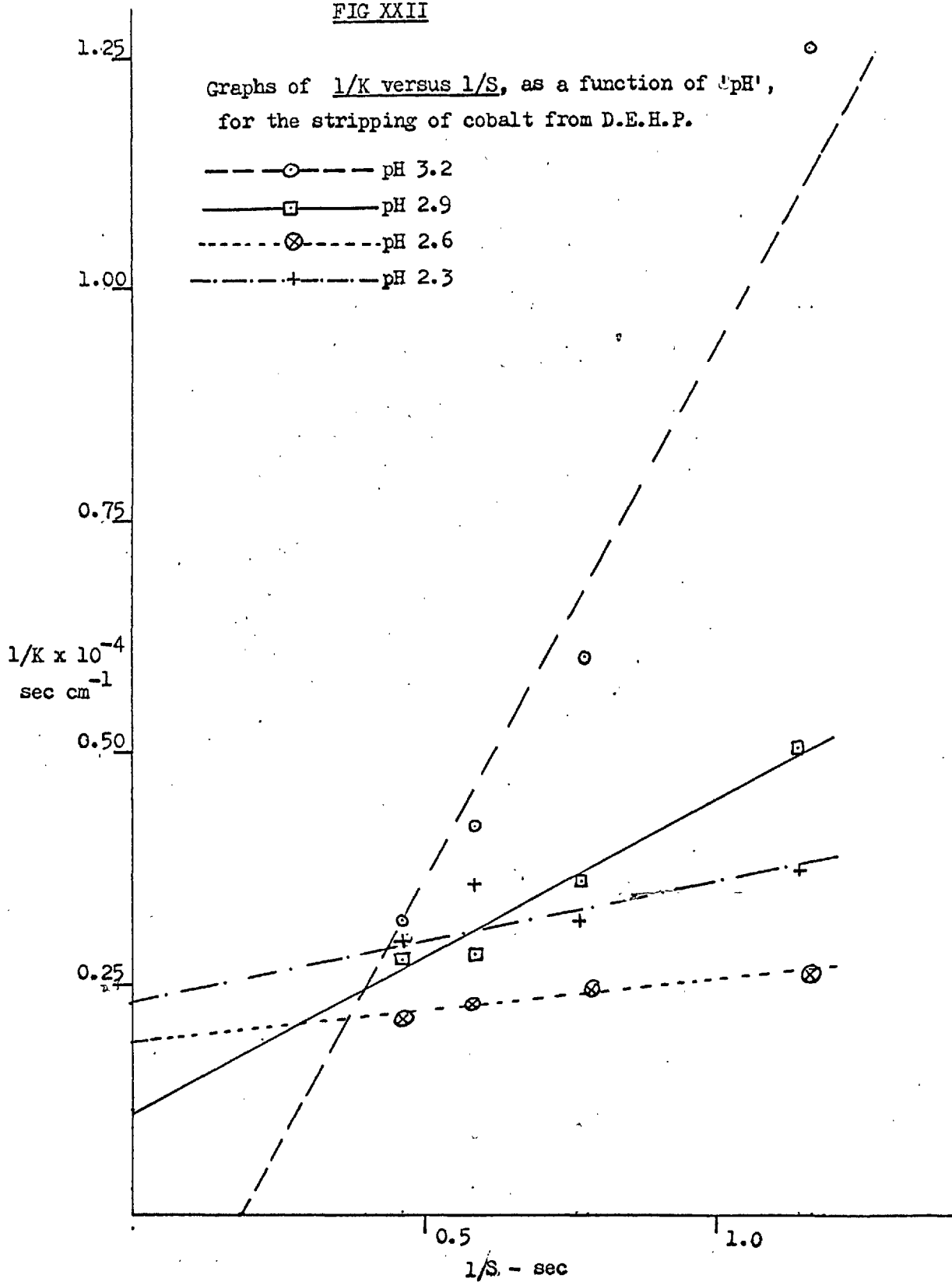


FIG XXIII

Graphs of $1/K$ versus $1/S$, as a function of 'pH', for the stripping of nickel from D.E.H.P.

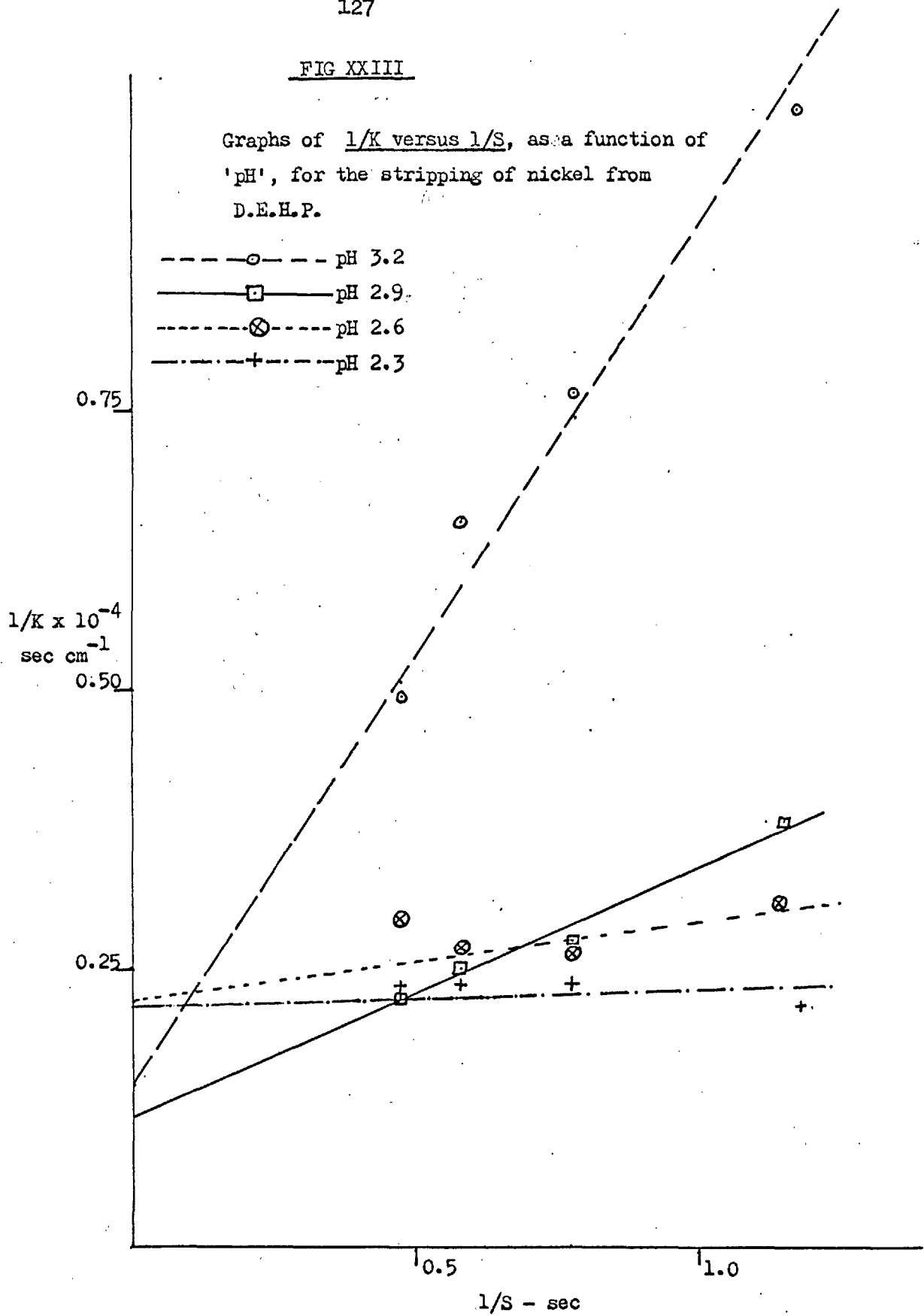


FIG XXIV

Graphs of $1/K$ versus $1/S$, as a function of temperature, for the stripping of copper from D.E.H.P.

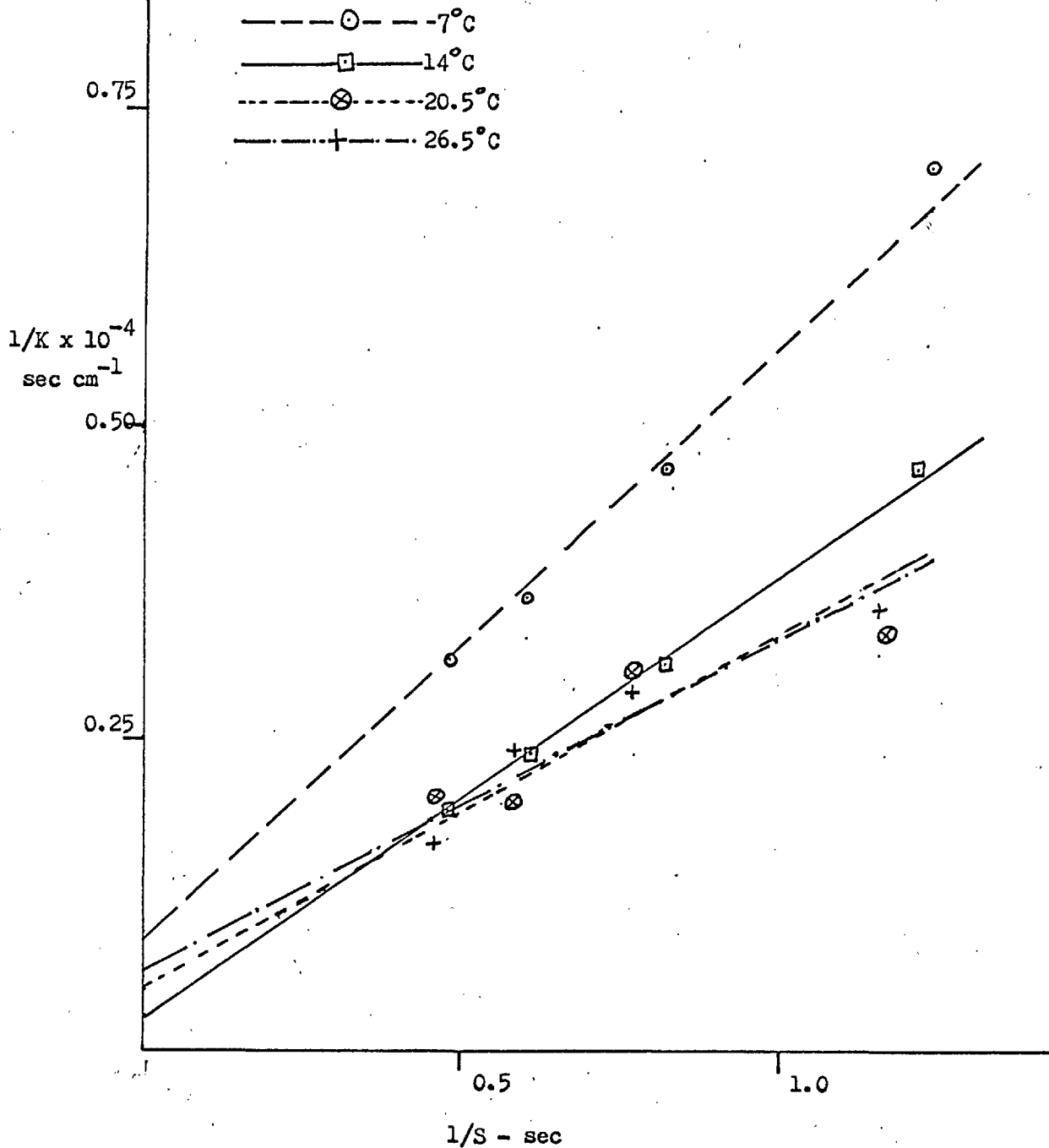


FIG XXV

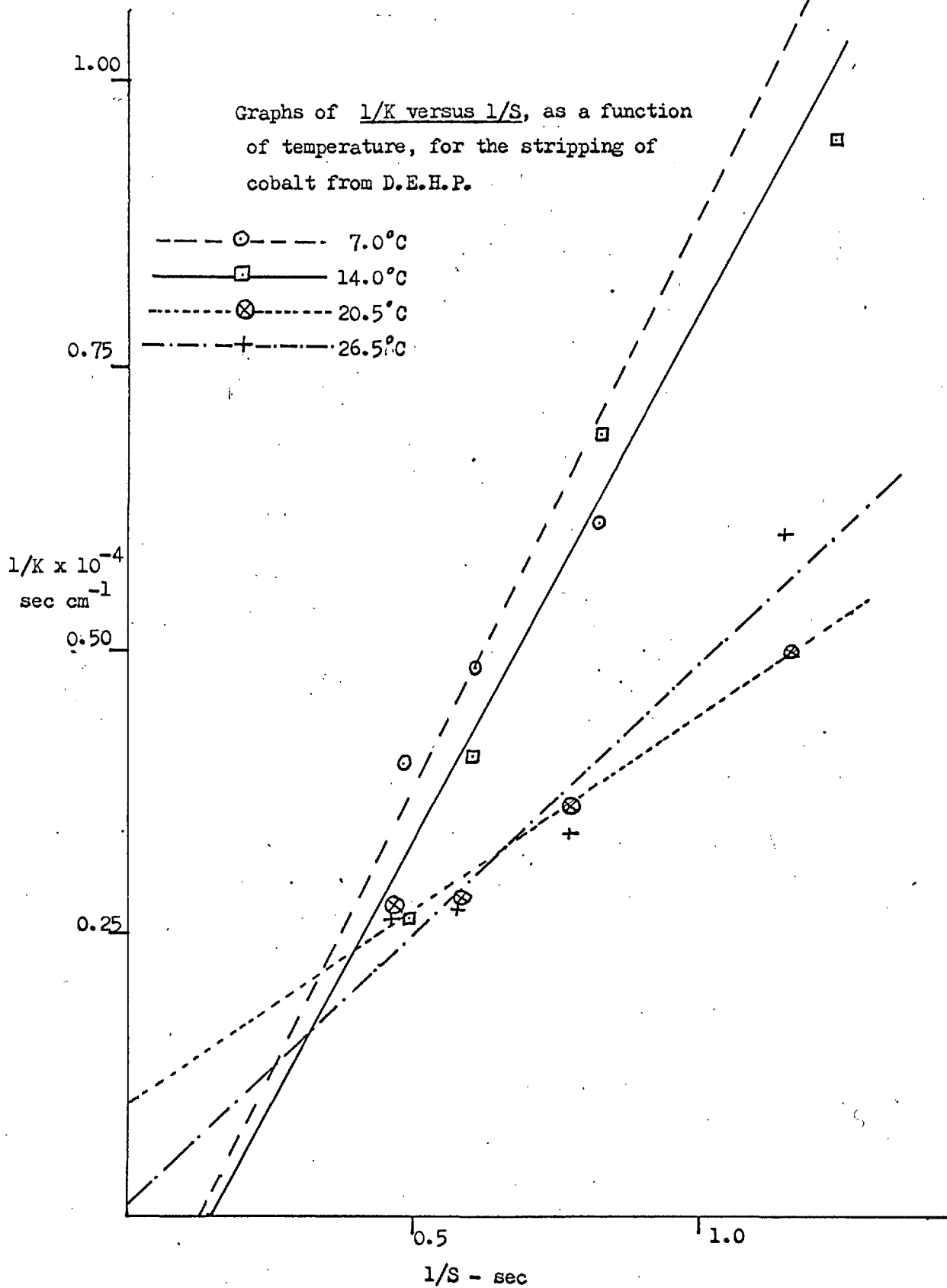


FIG XXVI

Graphs of $1/K$ versus $1/S$, as a function of temperature, for the stripping of nickel from D.E.H.P.

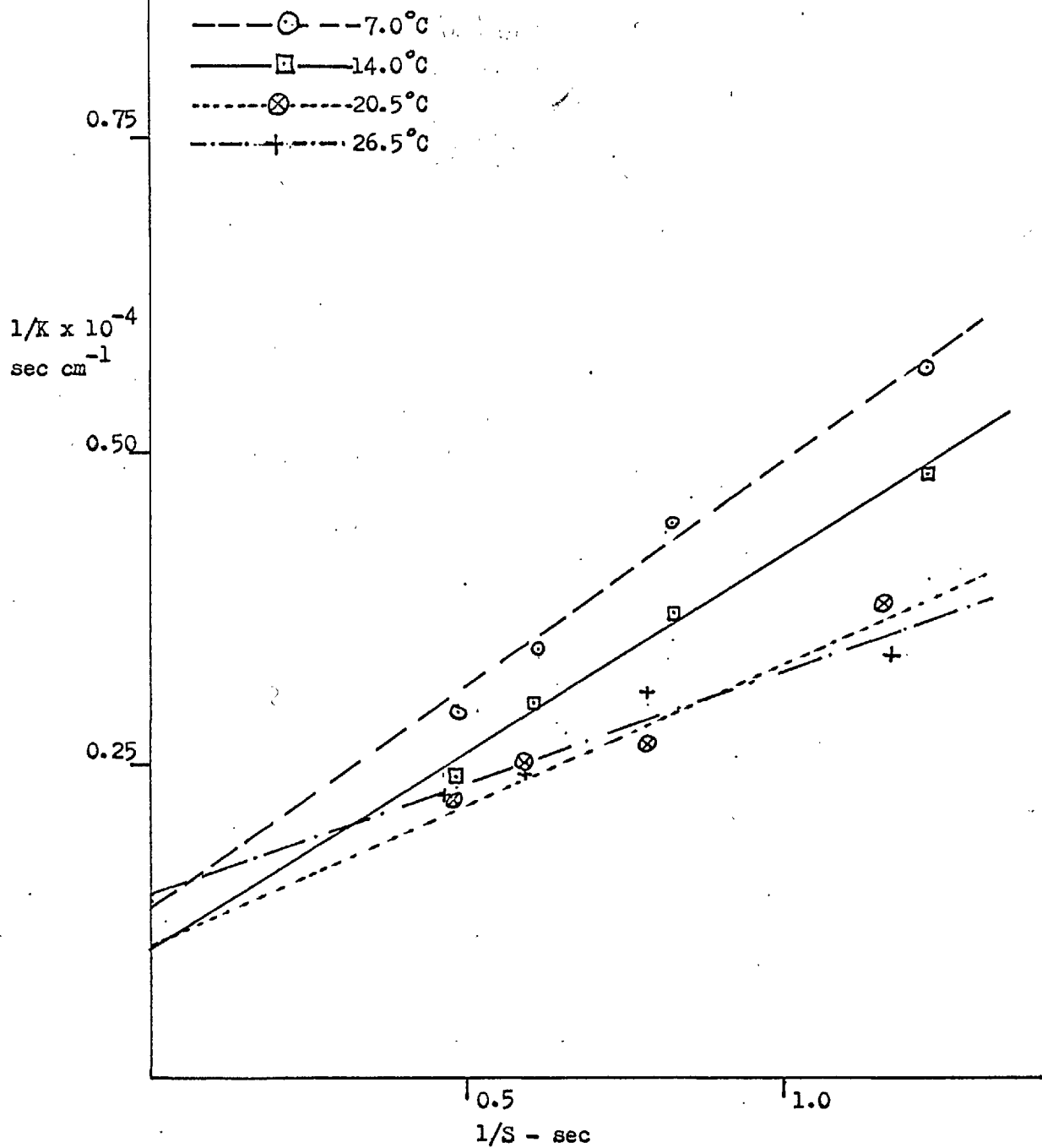
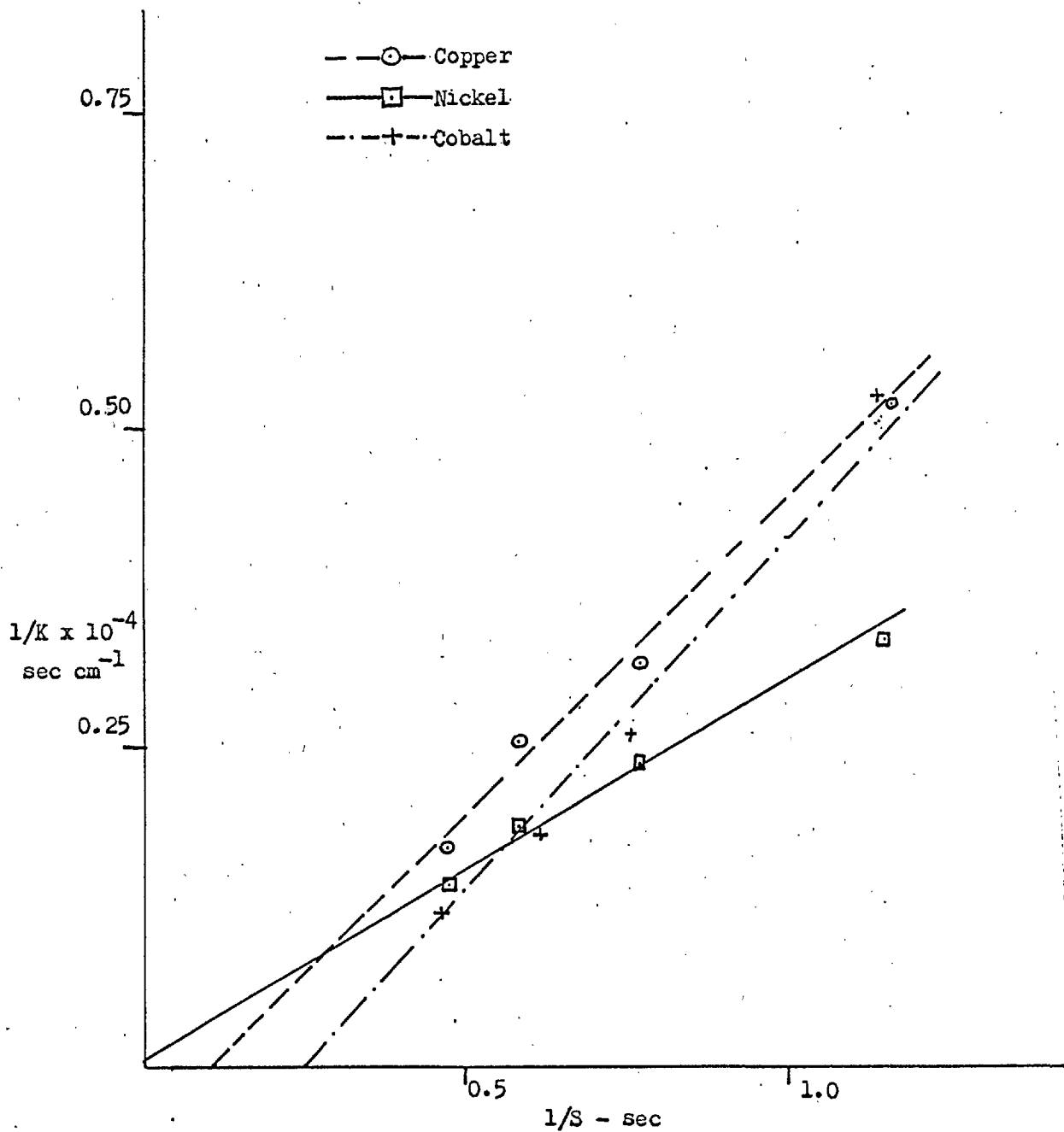


FIG XXVII

Graphs of $1/K$ versus $1/S$ for the stripping of copper cobalt and nickel from D.E.H.P. With capryl alcohol present.



3.3 RESULTS OF VISCOSITY DETERMINATIONS

The reasons for these measurements and details of the experimental method used have already been given on page 46 . In Table IXL values of the viscosity η and the kinematic viscosity ν are given for the organo-metallic complex solutions used; the effect of metal concentration, D.E.H.P. concentration and capryl alcohol were investigated.

TABLE IXL

(a) Copper

D.E.H.P. Conc.M	CpOH Conc.M	Copper Conc. x 10^3 M	η Centipoise	ν $\text{cm}^2 \text{sec}^{-1} \times 10^2$
0.2	-	20.0	1.39	1.75
0.2	-	15.0	1.40	1.76
0.2	-	8.0	1.41	1.78
0.2	-	5.0	1.40	1.76
0.4	-	9.0	1.57	1.97
0.1	-	9.0	1.27	1.61
0.05	-	8.0	1.24	1.58
0.1	0.5	8.0	1.80	2.28

[CpOH = capryl alcohol]

(b) Cobalt

D.E.H.P. Conc.M	CpOH Conc.M	Cobalt Conc. x 10^3 M	η Centipoise	ν $\text{cm}^2 \text{sec}^{-1} \times 10^2$
0.1	-	18.0	1.97	2.49
0.1	-	12.0	1.96	2.48
0.1	-	7.0	1.99	2.51
0.1	-	5.0	1.98	2.50
0.4	-	8.0	2.39	3.00
0.2	-	8.0	2.06	2.60
0.05	-	4.0	1.88	2.36
0.1	0.5	7.0	1.68	2.13

(c) Nickel

D.E.H.P. Conc.M	CpOH Conc.M	Nickel Conc. x 10 ³ M	η Centipoise	$\text{cm}^2 \text{sec}^{-1} \times 10^2$
0.2	-	12.0	1.42	1.79
0.2	-	10.0	1.38	1.74
0.2	-	6.0	1.39	1.75
0.2	-	3.0	1.39	1.75
0.4	-	7.0	1.59	2.00
0.1	-	6.0	1.39	1.75
0.05	-	4.0	1.35	1.71
0.1	0.5	5.0	1.79	2.27

(d) Without Metal

D.E.H.P. Conc.M	CpOH Conc.M	η Centipoise	$\text{cm}^2 \text{sec}^{-1} \times 10^2$
0.4	-	1.42	1.79
0.2	-	1.27	1.60
0.1	-	1.18	1.49
0.05	-	1.15	1.46
0.1	0.5	1.55	1.97

3.4 RESULTS OF DIFFUSION COEFFICIENT MEASUREMENTS IN ORGANIC SOLUTIONS

The reasons for these measurements and the experimental techniques used are given on page 47/8. In Table XL the experimental results are given and compared with values calculated from Einstein's formula (page 47) using the viscosity data of pages

D.E.H.P. Conc	Metal Conc.M	D. Exp $\text{cm}^2 \text{sec}^{-1} \times 10^6$	D.(Einstein) $\text{cm}^2 \text{sec}^{-1} \times 10^6$
0.2	0.012 Ni	2.04	1.46
0.2	0.003 Ni	2.11	1.46
0.05	0.004 Ni	2.13	1.63
0.2	0.020 Cu	1.80	1.56
0.2	0.006 Cu	0.92	1.56
0.05	0.008 Cu	2.38	1.76
0.1	0.007 Co	1.41	1.18
0.2	0.008 Co	1.24	1.14

3.5 RESULTS OF MEASUREMENTS OF INTERFACIAL TENSION BETWEEN AQUEOUS SOLUTIONS AND PARAFFIN SOLUTIONS CONTAINING D.E.H.P. AND METAL COMPLEXES

The details of the experimental method used for these determinations was given on page 46. The results obtained are given in Table XLI (a - e).

TABLE XLI
(a) D.E.H.P. alone

D.E.H.P. Conc.M	H ₂ SO ₄ Conc.M	pH	γ dynes cm ⁻¹ .
0	0	5 approx	49.7
0.05	0	"	26.4
0.1	0	"	23.9
0.2	0	"	22.1
0.4	0	"	20.4
0.1	4×10^{-4}	3.10	24.0
0.1	10^{-3}	2.70	24.7
0.1	3×10^{-3}	2.25	25.0
0.1	10^{-2}	1.90	25.2
0.05	4×10^{-4}	3.10	26.5
0.05	10^{-3}	2.70	26.6
0.05	3×10^{-3}	2.25	26.9
0.05	10^{-2}	1.90	27.4

(b) D.E.H.P. + copper complex

D.E.H.P. Conc. M	Metal Conc. M $\times 10^3$	H ₂ SO ₄ Conc. M	pH	γ dynes cm ⁻¹
0.2	20.0	10 ⁻³	2.70	19.2
0.2	15.0	10 ⁻³	2.70	19.4
0.2	9.0	10 ⁻³	2.70	19.7
0.2	6.0	10 ⁻³	2.70	20.9
0.4	9.0	10 ⁻³	2.70	20.2
0.1	8.0	10 ⁻³	2.70	19.5
0.05	8.0	10 ⁻³	2.70	18.9
0.1	8.0	0	5 approx.	19.2
0.1	8.0	4 $\times 10^{-4}$	3.10	19.8
0.1	8.0	3 $\times 10^{-3}$	2.25	21.1
0.1	8.0	10 ⁻²	1.90	23.4

(c) D.E.H.P. + nickel complex

D.E.H.P. Conc. M	Metal Conc. M $\times 10^3$	H ₂ SO ₄ Conc. M	pH	γ dynes cm ⁻¹
0.2	12.0	10 ⁻³	2.70	11.6
0.2	9.5	10 ⁻³	2.70	12.2
0.2	7.0	10 ⁻³	2.70	14.0
0.2	2.5	10 ⁻³	2.70	17.3
0.4	7.0	10 ⁻³	2.70	15.7
0.1	8.0	10 ⁻³	2.70	10.9
0.05	8.0	10 ⁻³	2.70	10.5
0.05	8.0	0	5 approx.	9.95
0.05	8.0	4 $\times 10^{-4}$	3.10	10.2
0.05	8.0	3 $\times 10^{-3}$	2.25	15.2
0.05	8.0	10 ⁻²	1.90	24.3

(d) D.E.H.P. + cobalt complex

D.E.H.P. Conc. M	Metal Conc. M. x 10^{-3}	H ₂ SO ₄ Conc. M	pH	γ dynes cm ⁻¹
0.1	18.0	10^{-3}	2.70	11.5
0.1	12.0	10^{-3}	2.70	13.1
0.1	7.0	10^{-3}	2.70	14.6
0.1	4.5	10^{-3}	2.70	16.6
0.05	8.0	10^{-3}	2.70	12.8
0.2	8.0	10^{-3}	2.70	16.6
0.4	8.0	10^{-3}	2.70	18.3
0.1	8.0	0	5 approx.	13.9
0.1	8.0	4×10^{-4}	3.10	13.9
0.1	8.0	3×10^{-3}	2.25	16.7
0.1	8.0	10^{-2}	1.90	23.5

(e) In the presence of capryl alcohol

CpOH 0.5 M; D.E.H.P. 0.1 M; H₂SO₄ 10^{-3} M; pH 2.70

Metal Conc. x 10^3 M	γ dynes cm ⁻¹	γ (Same Conditions no CpOH) dynes cm ⁻¹
0	17.4	24.7
7.0 (Cu)	15.8	19.8
7.0 (Ni)	12.9	11.9
7.0 (Co)	12.4	14.6

The data of Table XLI are illustrated by figures XXVIII - XXX and are summarised as follows:-

- (a) In the absence of any metal complex, an increase of D.E.H.P. concentration causes a decrease in interfacial tension. This can be expressed in terms of the Gibbs adsorption isotherm

$$\Gamma = (-C/RT)(d\gamma/dC) \quad 170.$$

$$\text{i.e. } \Gamma = (-1/(2.303 RT))(d\gamma/d \log C) \quad 171.$$

where Γ is the surface excess in moles/cm²

The results in Table XLIIa are plotted in Figure XXXI as γ versus $\log C$. From the limiting slope at high values of $\log C$ and equation 171, Γ was calculated to be 1.0×10^{-10} moles/cm². This value of Γ may also be expressed as one molecule per $160 (\text{Å}^{\circ})^2$. The D.E.H.P. molecule has two branched chain hydrocarbon groups, so its minimum cross-sectional area is expected to be approximately $50 (\text{Å}^{\circ})^2$, i.e. some $100(\text{Å}^{\circ})^2$ of the surface is available for adsorption of the metal complex into the interface.

- (b) With all three metals, an increase in metal concentration causes a further decrease in interfacial tension, i.e. the metal complex is more surface active than the D.E.H.P. The three metals increase in surface activity in the order $\text{Cu} < \text{Co} < \text{Ni}$.
- (c) At constant metal concentration, an increase in D.E.H.P. concentration causes a rise in interfacial tension, though the value is still lower than that in the absence of metal complex, i.e. the area available for metal complex adsorption is reduced.
- (d) With a decrease in pH, the interfacial tension increases in the presence of the metal complex and approaches that in the absence of a metal complex, showing that at least some of the adsorbed metal complex is converted immediately to D.E.H.P. However, even at pH 1.9, when the equilibrium is more than 30:1 in favour of the aqueous phase for all

Graphs of γ versus Metal Concentration
at pH 2.7.

- × Copper- 0.2 mole/litre D.E.H.P.
- Cobalt- 0.2 mole/litre D.E.H.P.
- ⊕ Nickel- 0.1 mole/litre D.E.H.P.

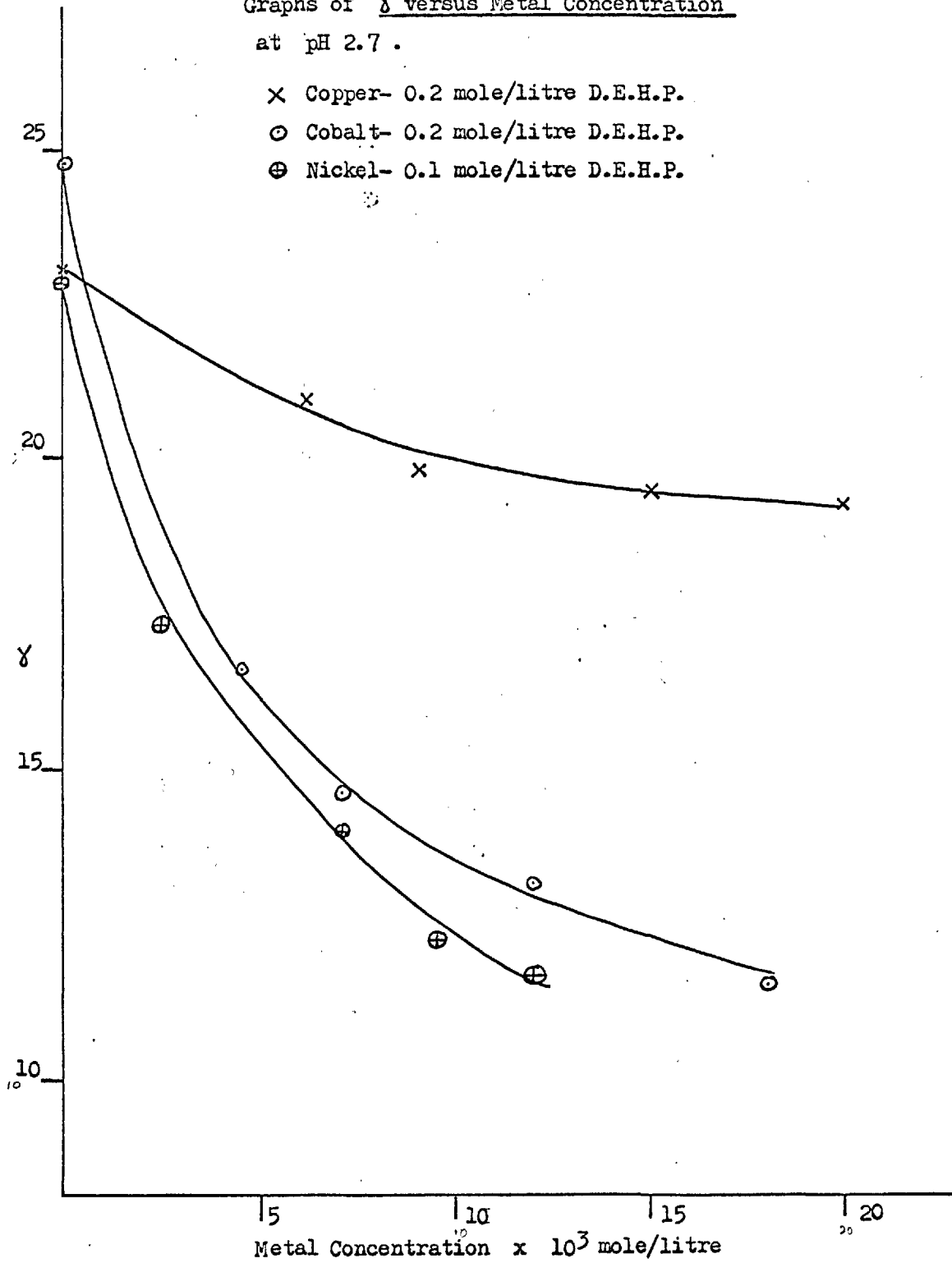


FIG. XXIX

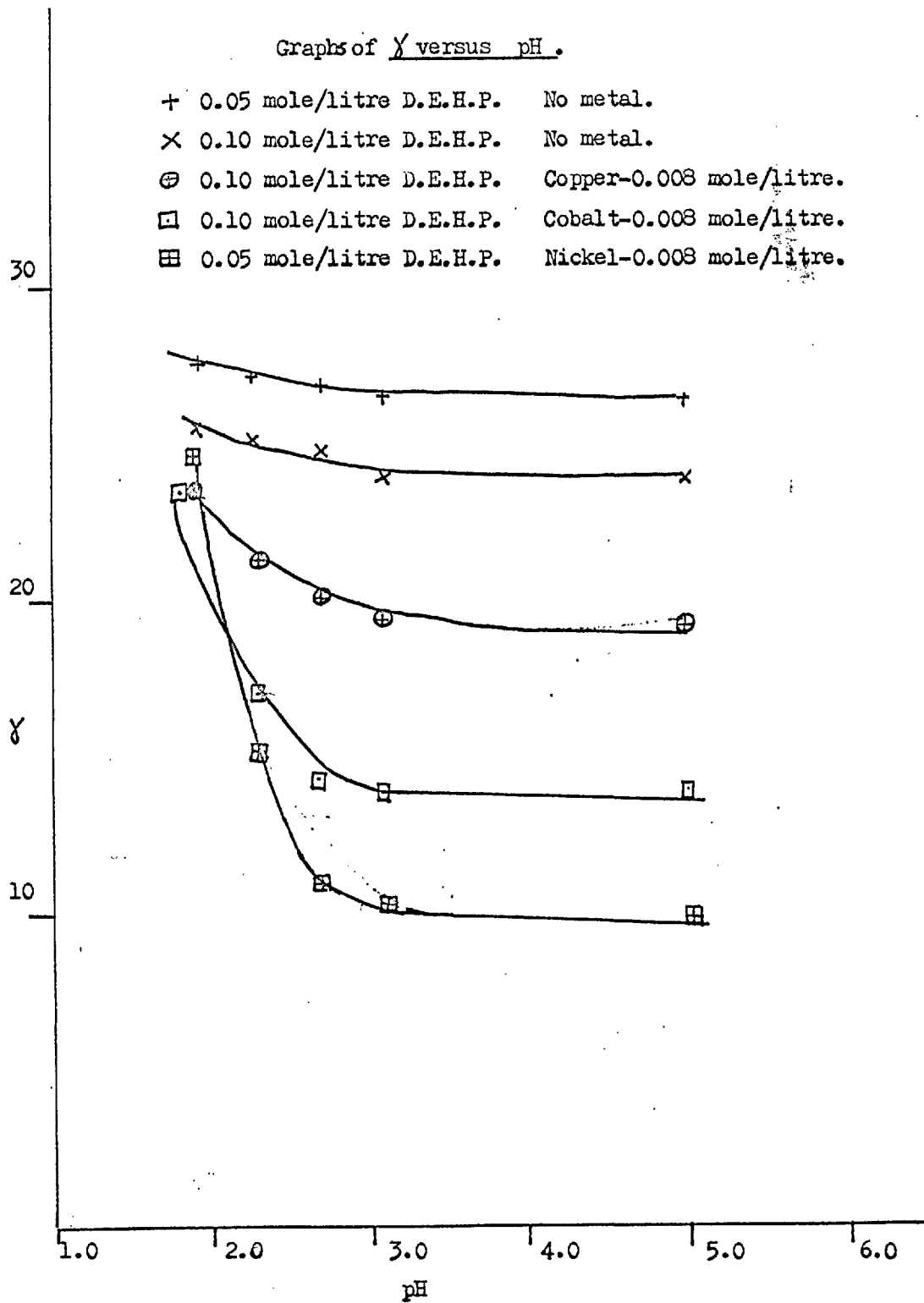


FIG. XXX

Graphs of γ versus D.E.H.P. Concentration at pH 2.7 .
(pH 5.0 approx for D.E.H.P. alone.)

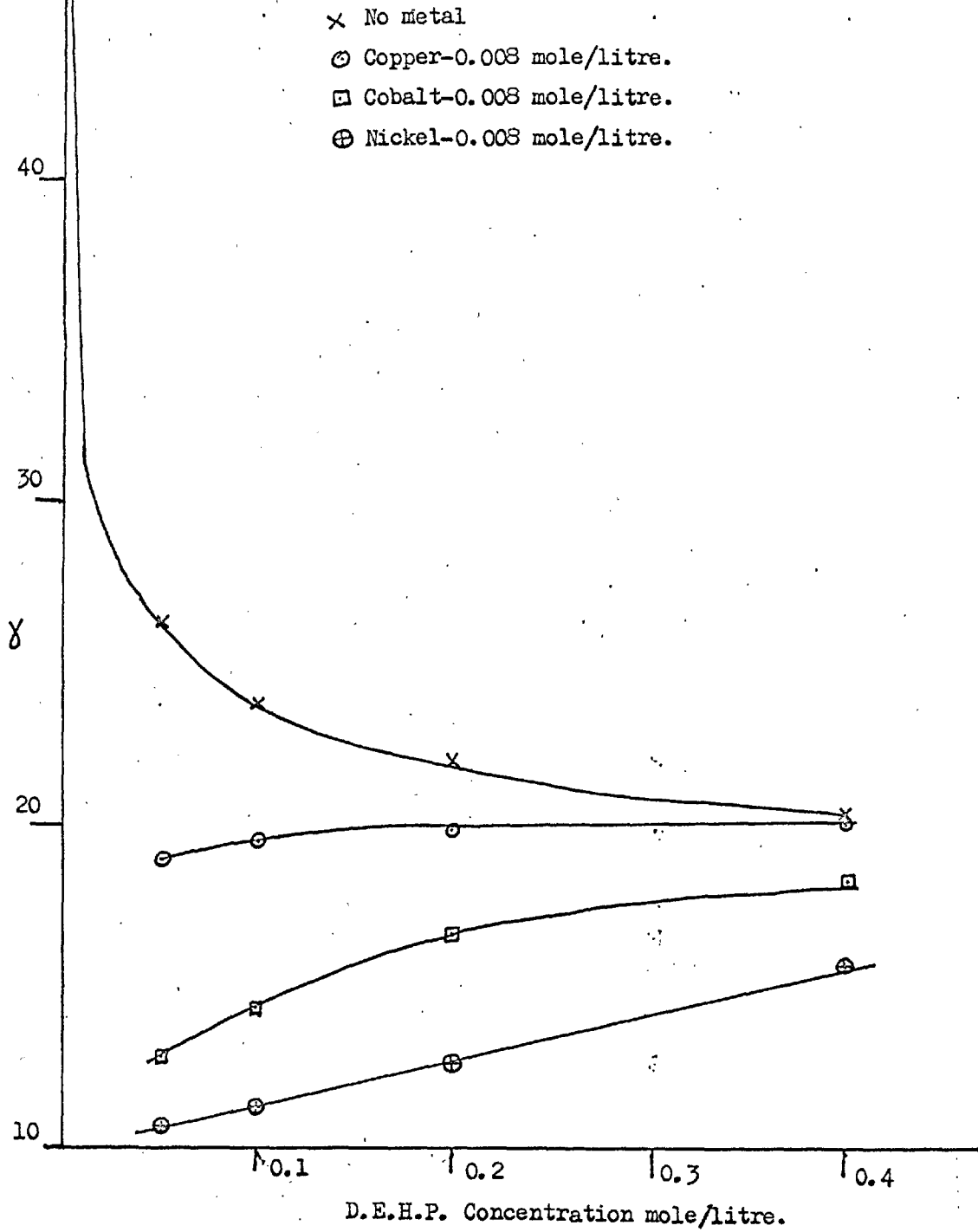
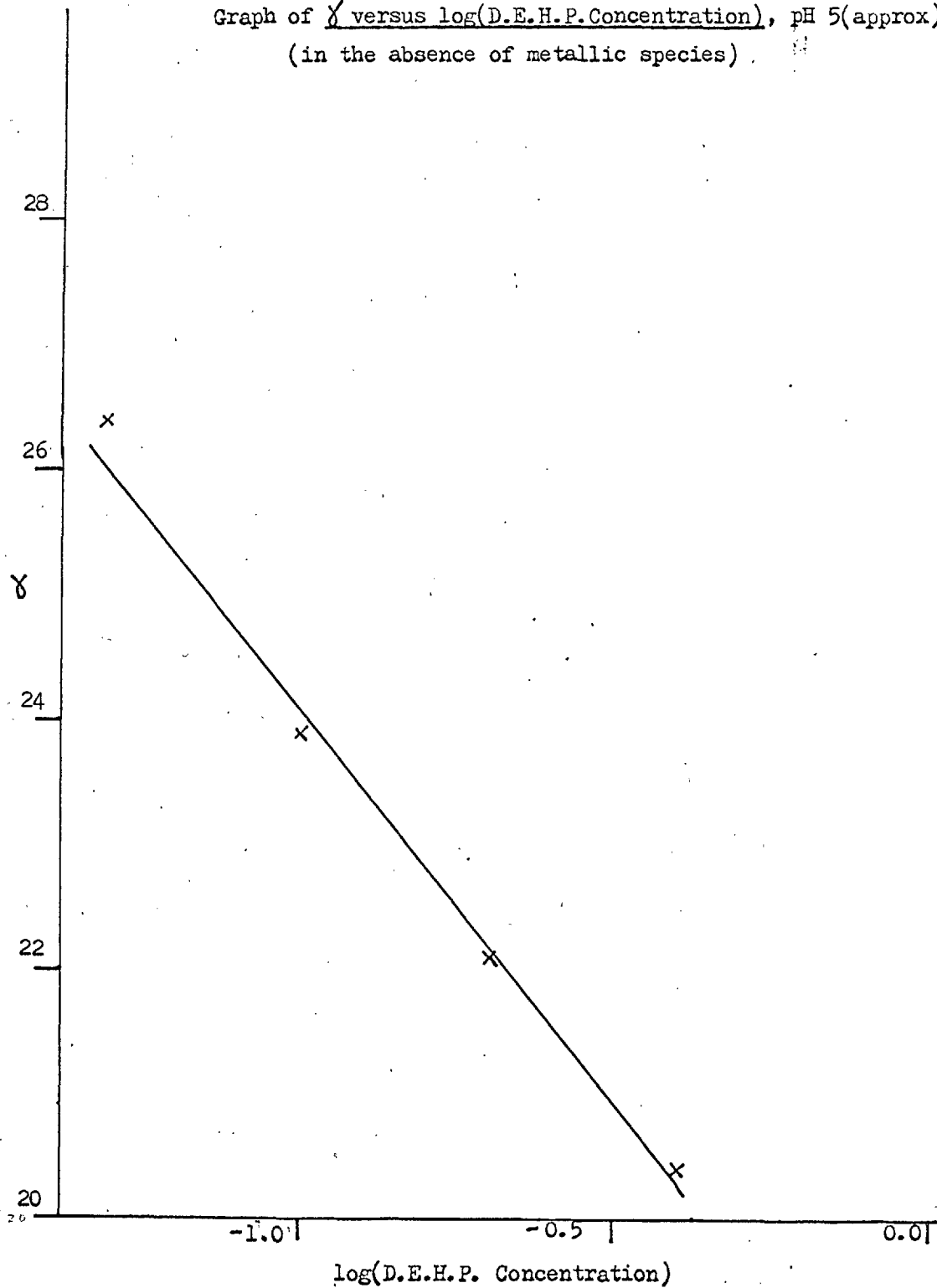


FIG. XXXI

Graph of γ versus $\log(\text{D.E.H.P. Concentration})$, pH 5 (approx).
(in the absence of metallic species).



three metals, the interfacial tension is still lower than that for D.E.H.P. alone, i.e. not all of the adsorbed metal complex is immediately converted. The interfacial tension, with D.E.H.P. alone, changes little with pH. This is to be expected since, over the pH range investigated, the D.E.H.P. is unionized.

- (e) In the presence of capryl alcohol, with no metal complex, there is a considerable lowering in the interfacial tension due to the adsorption of this reagent. With the metal complex present, there is a smaller change in the interfacial tension than in the absence of capryl alcohol. This result is similar to that found with high concentrations of D.E.H.P. and is caused by swamping the effect of the metal complex.

N.B. In none of the interfacial tension measurements was there any evidence of drop oscillation as might be expected if 'excessive' or 'marked' spontaneous interfacial turbulence was present.

4.

DISCUSSION OF RESULTS AND CONCLUSIONS

The kinetic aspects of this thesis can be divided into two broad sections. In the first section, in which the hydrodynamic characteristics of the cell design have been evaluated, the rate of transfer of 8-hydroxyquinoline from aqueous buffer solutions into paraffin has been studied under varying conditions of stirring rate, interfacial area, temperature and aqueous concentration of 8-hydroxyquinoline. By judicious choice of the pH of the aqueous solutions, such that the 8-hydroxyquinoline was in the unionized state in both the aqueous and organic phases, it is felt to be a fair assumption that, for this system, no interfacial chemical reaction is involved and the overall rate of transfer is wholly governed by the rate of transfer to and from the interface.

4.1 EXTRACTION OF 8-HYDROXYQUINOLINE

A precise theoretical derivation of the rate of mass transfer in the system studied, by solution of the Navier-Stokes equations¹⁰⁵, is extremely difficult in view of the boundary conditions prevailing. Simplification of the problem to that of infinite rotating discs in a semi-infinite medium is not sound, as can easily be seen by examining Figures XXXII (a & b) which show the two velocity profiles. In the case of the finite cell, comparing the flow patterns near to the axis and near to the cylindrical walls, there is a reversal in the direction of the axial velocity (the velocity perpendicular to the interface), the direction of the axial velocity being away from the interface near to the axis of the cell and towards the interface near to the cell walls.

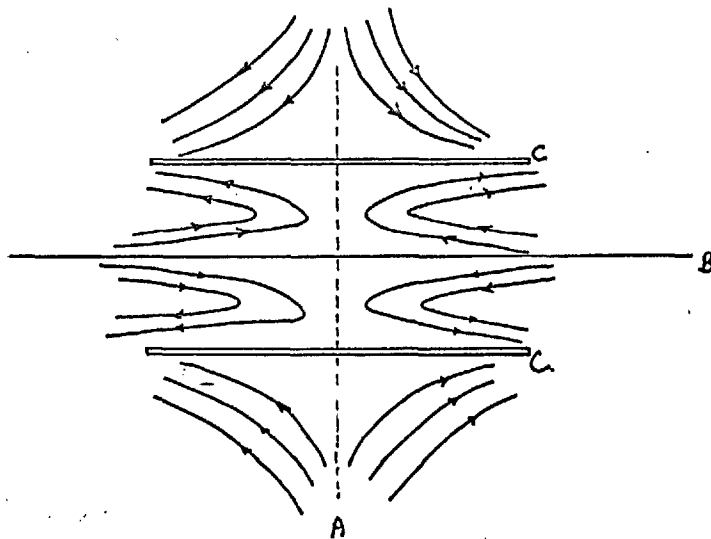
The variation of the tangential velocity from one disc to the other has been deduced by Stewardson¹⁰⁶ to be of the form shown in Fig. XXXIII(a), for two infinite discs rotating in opposite directions. Although Stewardson tested his theoretical results by experiments involving discs rotating in air, it is reasonable to assume that, for discs rotating in liquids, having Reynolds numbers of the same order as he used, the boundary layers near the discs will be of the same order as he found, i.e. approximately 0.5 cm.

[Solution of the Navier-Stokes equations for a single infinite disc, rotating in water at 1 rev/sec., gives a boundary layer of approximately 0.5 cm.]

FIG XXXII.

Radial and Axial flow patterns in a disc stirred, fixed interface, cell.

(A) Cell with infinite dimensions.



(A) Axis of Rotation.

(B) Interface.

(C) Stirrer Discs.

(B) Cell with finite dimensions.

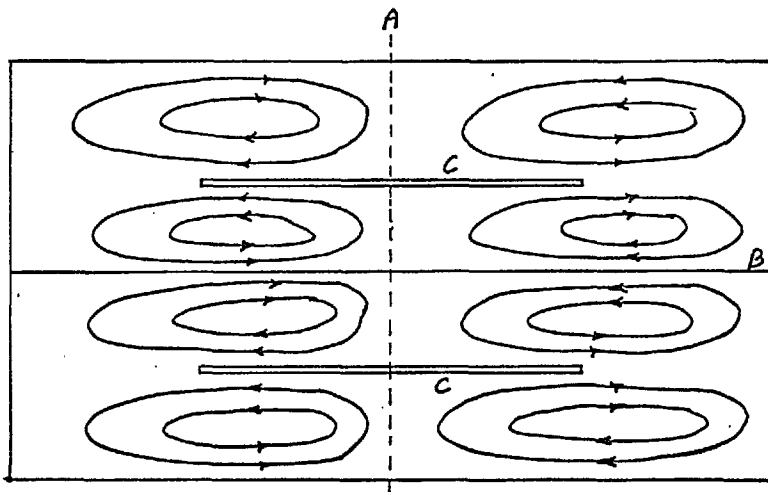
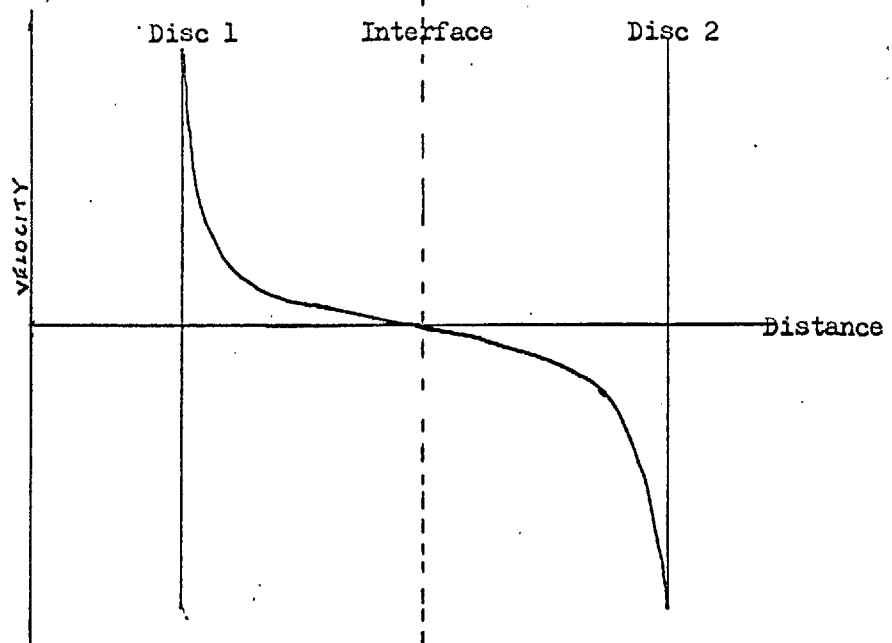


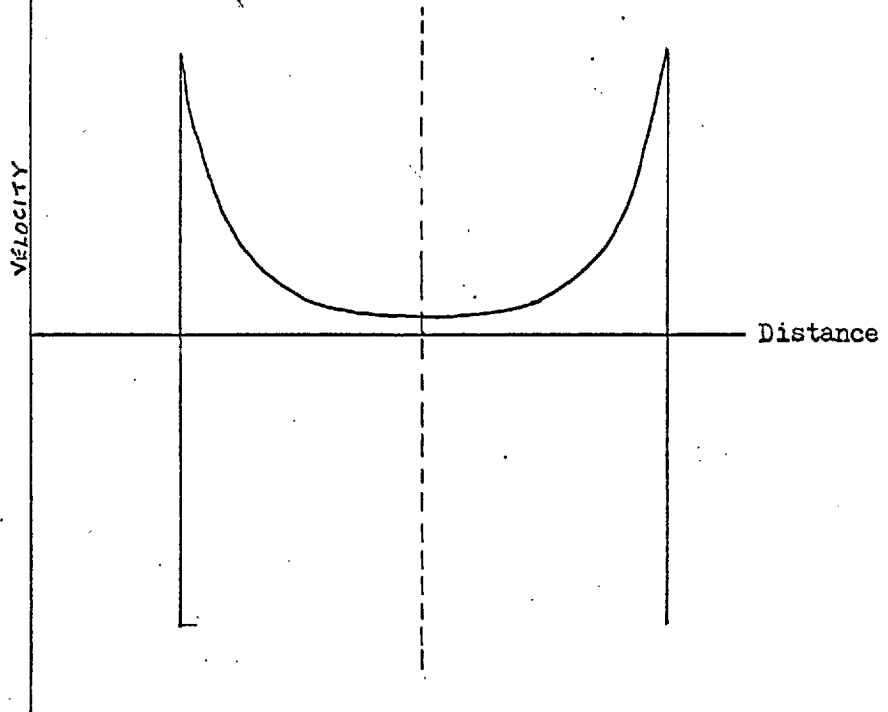
FIG XXXIII.

Tangential Velocity profiles between two rotating discs.

(A) Contra-rotating.

(after Stewardson¹⁰⁶)

(B) Co-rotating.



The effect of having two liquids of different viscosity, with the interface between the two discs, will be to move the position of zero tangential velocity away from the mid point between the discs (the position if the discs rotate at the same speed in a single medium).

The displacement of this point will depend on the relative kinematic viscosities of the two fluids. The tangential velocity profile for two co-rotating discs has also been studied by Stewardson¹⁰⁶ and is shown in Fig. XXXIII(b). The ratio of the tangential velocity at the disc surface to that at the interfacial plane will depend on the nature of the liquids and the distance separating the discs. Olander⁹⁵ reported this to be of the order of 10/1 for a cell of similar design to that used in this work.

There is no reason to suppose that the finite boundary limits imposed by the confines of the cell will seriously alter the tangential velocity profiles shown in Fig. XXXIII. However, the variation of the radial and axial velocities from the centre of rotation to the cell walls will no longer follow the relationship found for infinite discs, i.e. radial velocity proportional to the radial distance and axial velocity independent of radial distance. In fact, the relationship will become far more complex.

If

V_{θ} = Tangential velocity cm. sec⁻¹

V_r = Radial velocity cm. sec⁻¹

V_x = Axial velocity cm. sec⁻¹

θ , x & r being the corresponding co-ordinates

R is the radius of the disc cm.

R^1 " " " " " cell cm.

S is the rate of rotation of the discs rev./sec⁻¹

d is the distance of the discs from the interface

then the boundary conditions imposed by the cell can be expressed by the following relationships:-

$r \rightarrow 0$; $V_r \rightarrow 0$, $V_{\theta} \rightarrow 0$,

$r \rightarrow R^1$; V_r , V_x and $V_{\theta} \rightarrow 0$.

$x = 0$ (at the interface) $V_{\theta} \rightarrow 0$.

$dV_{\theta}/dx \rightarrow 0$.

$V_r \rightarrow 0$.

$V_x \rightarrow 0$.

$x = d$ $V_r \rightarrow 0$

$V_x \rightarrow 0$.

$x = d$ From $r = 0$ to $r = R$

$V_{\theta} = 2\pi S r$

From $r = R$ to $r = R^1$

V_{θ} reduces to zero again and the relationship

between V_θ and r will have the same form as the variation of tangential velocity between the fixed and rotating cylinders of a rotating cylinder viscometer.

The equations and velocity profiles given above assume laminar flow, which is reasonable for discs with Reynolds number below 10^4 .

(The Reynolds number is defined by $Re = R^2 S \rho / \eta$.)

No method has been found for solving the Navier-Stokes equations analytically with the above boundary conditions. The only possible way of solving this problem would appear to be to produce actual numerical velocity profiles, by use of an analogue computer, and to fit algebraic equations to these over a narrow range of system parameters. Once obtained, the velocity profiles may be used to solve the steady state diffusion equation 107:-

$$V_x \frac{dc}{dx} + V_r \frac{dc}{dr} = D \left[\left(\frac{d^2c}{dx^2} \right) + \left(\frac{d^2c}{dr^2} \right) + \left(\frac{1}{r} \right) \left(\frac{dc}{dr} \right) \right] \quad 172.$$

Since a precise mathematical model for mass transfer in this cell could not be derived, relationships of an empirical nature have had to be found and compared with the results of other workers using similar cells.

4.1.1. Kinetic Results for 8-hydroxyquinoline

The kinetic results for 8-hydroxyquinoline can be expressed by the following relationship:-

$$K = (a_0 + b_0 S) \exp (-E/RT) \quad 173.$$

where K is the mass transfer coefficient, S the stirring rate, E the activation energy and a_0 and b_0 are constants. It was also found that the rate of mass transfer per unit area was independent of the position of the area with reference to the stirrer shaft and cell boundaries. This relationship concerning the interfacial area does not appear to have been determined experimentally by other workers. Olander⁹⁵ attempted to obtain a theoretical model of a similar cell by making a large number of assumptions and solving the Navier-Stokes equations with these assumptions. One of these assumptions was that all the liquid under the stirrers was moving in solid body rotation. This appears to be unjustified, since the tangential velocity between the interface and the discs is very small, except in the boundary layer near the discs (page 143). Olander's model showed that, underneath the stirrers, the concentration gradient at the interface was zero and hence no transfer could take place; transfer being confined to the interfacial area outside the compass of the stirrers.

This result has been disproved by the above experimental data, at least in the case of the cell used in these experiments. Another assumption Olander made was that radial movement of the fluid played no part in mass transfer, i.e. he reduced equation 172 to a single dimension.

The relationship between stirrer speed and mass transfer can be compared with other experimental work, although, here again, no precise parallel is available. Both Lewis^{65,66} and McManamey⁹⁴ have attempted to obtain a general empirical relationship for a number of extractant systems in terms of dimensionless groups. These relationships were:

$$60 k_A \sqrt{V_A} = \alpha (Re_A + Re_B \eta_B / \eta_A)^{1.65} + 1 \quad 174.$$

$$\text{and } 60 k_A \sqrt{V_A} = \alpha (Sc_A)^{-0.37} (Re_A)^{0.9} (1 + \eta_B Re_B / \eta_A Re_A) \quad 175.$$

respectively.

These equations were obtained by log/log plots of the dimensionless groups against mass transfer rate and the powers found from the best straight lines. Reducing the above equations to the simple form of a single system with both stirrers rotating at the same speed, the relationships between mass transfer coefficient and stirrer speed (S) became

$$k_A = \beta \left[(2\pi SR / \eta_A) (\sigma_A + \sigma_B) \right]^{1.65} + \sqrt{V_A} / 60 \quad 176.$$

i.e. $k_A \propto S^{1.65}$ for Lewis's equation

$$\text{and } k_A = \beta (2\pi SR / \eta_A)^{0.9} (1 + \sigma_B / \sigma_A) \quad 177.$$

i.e. $k_A \propto S^{0.9}$ for McManamey's equation.

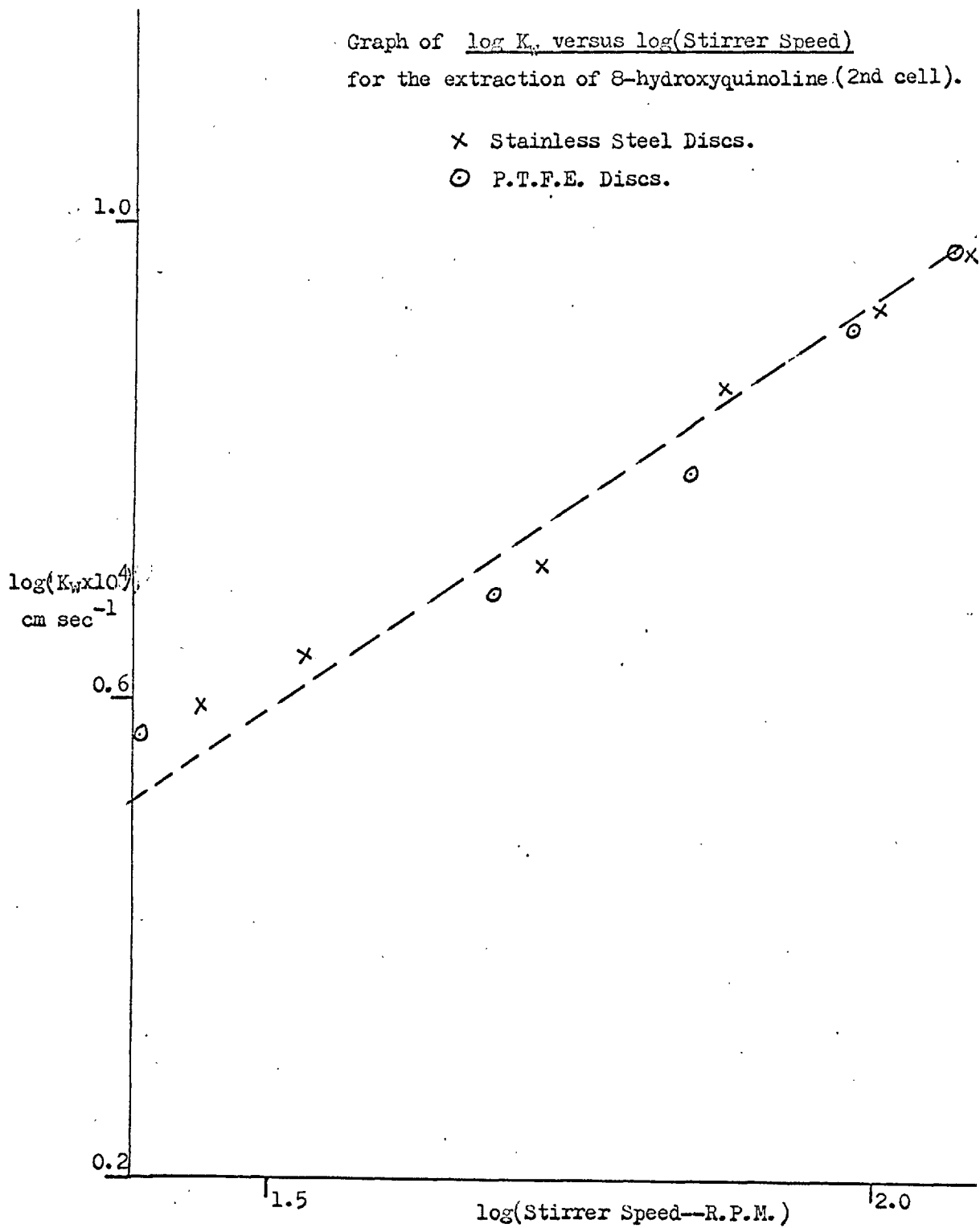
Neither of these equations has a true constant part (the constant $\sqrt{V_A}$ in Lewis's equation being part of an approximation), i.e. $[k_A = A + BS^n]$, and such a factor could not have been found by use of log/log plots.

For comparison a log/log plot of mass transfer coefficient against stirring speed for 8-hydroxyquinoline, using the results of Tables XI and XII (pages 77 & 78), has been drawn in Fig. XXXIV. Neither of the graphs shows a good straight line fit and the relationship

$$K = a + bS \quad 178.$$

is a much more accurate way of expressing the variation of mass transfer with stirring speed than an equation of the type

$$K \propto S^n \quad 179.$$

FIG XXXIV

It is expected that the application of hydrodynamic and diffusion theory, as outlined on pages 143-147, would lead to relations similar to those found experimentally between stirring speed, interfacial area and mass transfer rate. However, this theory does not include the possibility of an interfacial resistance. The simplest way to include this possibility is to assume that the presence of an interfacial resistance does not alter the resistance to mass transfer, by diffusion in the two phases. The effective resistance is then simply the sum of the interfacial and diffusion resistances which leads to the relation:

$$1/K = 1/K_w + 1/K_c \quad 180.$$

where $1/K$ is the overall resistance, $1/K_c$ the interfacial resistance and $1/K_w$ the diffusion resistance, which, as has been shown above, can be represented by $1/(a + bS)$.

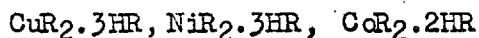
Assuming that any interfacial resistance is independent of stirring speed (an assumption commonly made in chemical kinetics, i.e. the rate of a chemical reaction or adsorption is independent of agitation), a simple straight line relationship between $1/K$ and $1/S$ can be made assuming that a is small compared with bS . (This would appear to be a fair assumption except at low stirring speeds.) For this reason, the lowest stirring speed used in measuring the rate of the stirring reactions was not used in plotting graphs of $1/K$ against $1/S$. (Other reasons were given on page 100.)

4.2 THE STRIPPING OF COPPER, NICKEL AND COBALT FROM DI-(2-ETHYLHEXYL)-PHOSPHORIC ACID

4.2.1 Equilibrium Studies

Before discussing the kinetic results obtained on these systems some consideration should be given to the results of the equilibrium studies and also to the limitations of the method of the analysis used for the kinetic measurements.

The equilibrium studies served a two-fold purpose: firstly, to give values of the distribution coefficients for use in the interpretation of the kinetic measurements (see page 88): secondly, the results of the studies have also been used to obtain an insight into the nature of the metal-organic complexes. In view of the lack of knowledge of the activity coefficients of organic species, this method obviously has considerable limitations and the formulae obtained, viz. (page 56)



must be used with caution.

These formulae will certainly only apply at low metal concentrations and low metal to phosphate ratios in the organic phase, and the number of neutral molecules that are bonded to the complex, in the case of copper or nickel, seems unrealistic; three neutral acid molecules bonded to the complex give a co-ordination number of five which is difficult to reconcile to the known chemistry of these two metals. A co-ordination number of four, such as that of the cobalt complex, is more likely, although three or six are also possibilities. It should be remembered, however, that these molecular formulae have been determined by reducing the slopes of log/log plots to their nearest whole numbers and hence their accuracy is very limited. It is not justifiable to make any further conclusions, based on the equilibrium results, as to the bonding and structure of the complex.

Although the equilibrium studies produced no evidence of polymerisation, it is almost certain that, at higher metal to phosphate ratios, the organic species will change to a polymer-like substance. Baes et al⁴ have shown, from viscosity measurements and maximum possible loadings, that the uranium complex with D.E.H.P., at high loadings, has a structure of the type $[(UO_2)R_2]_n 2HR$, with values of n from six upwards. Similar results have been obtained for the beryllium complex by Cattrall¹⁰⁸ and further confirmation was obtained by infra-red examination of the pure complex. The pure complex of copper butyl phosphate was found by Baldwin¹⁰⁹ to melt between 118°C and 119°C and cryoscopic determinations in diphenyl showed a molecular weight in excess of 10,000. This is equivalent to a polymer containing more than twenty organo-metallic groups.

4.2.2. Kinetic Results

The method used for the analysis of the kinetic results, although preferable to that used by McManamey⁷⁵ in analysing his results for the extraction of copper, nickel and cobalt nitrates, is still subject to severe limitations. In the groups of experiments in which variation of pH and D.E.H.P. concentration was studied, the kinetics of transfer changed from being dominated by the diffusional resistance to being dominated by the interfacial resistance. From the study of the statistical accuracy involved in the measurement of $1/K_c$ and $1/b$ (pages 93-97), it can be seen that only over very narrow limits can the values of both $1/K_c$ and $1/b$ be determined accurately and the range of values over which they are both statistically significant is only a little greater. (It should be borne in mind that $1/b$ and $1/K_c$ are related to a second differential of

the experimental, concentration versus time, data.) For this reason it is difficult to be certain of the precise effect of many of the variables on the value of the interfacial resistance over a wide range of values of the variables. However, some tentative conclusions can be drawn and these will now be discussed.

4.2.2.(a). Experimental Results

(Tables of results and graphs can be found between pages 97-118.)

(a) Influence of total metal concentration

The results and graphs for these runs are shown in Tables XIX-XXI and XXXIV and Figures XV to XVII. For all three metals the values of $1/K_c$ were found to be statistically insignificant. The relation between $1/b$ and metal concentration is of the same form as that deduced from the results for 8-hydroxyquinoline and equations 145-147 (page 91), i.e. $1/b$ increases with increase in metal concentration. However, the experimental values of $1/b$ are smaller than the theoretical values in all cases. Although significant determinations of $1/K_c$ were not possible for this set of runs, it is possible to conclude whether or not there is a marked trend of variation of $1/K_c$ with metal concentration. If $1/K_c$ were either proportional to or inversely proportional to the metal complex concentration, then with a 4-fold change of the latter, any change of $1/K_c$ should be quite apparent from the graphs of $1/K$ versus $1/S$. Inspection of Figures XX to XXII shows that there is not a four-fold change in the intercept $1/K_c$. Thus it is concluded that, within the range of metal concentrations studied and at the appropriate level of the other variables, no significant change of interfacial resistance occurs.

(b) Influence of D.E.H.P. concentration

The results and graphs for these runs are shown in Tables XXII-XXVI and XXXV and Figures XVIII-XX. For all three metals the variation of $1/b$ with D.E.H.P. concentration follows that predicted theoretically. Once again the experimental values are smaller than the theoretical values. The decrease in $1/b$ as the concentration of D.E.H.P. is reduced is sufficient to change the importance of $1/K_c$ from statistically insignificant to significant at the 1% level, whereas the significance of $1/b$ drops from significant at the 1% level to statistically

insignificant. With the concentration of D.E.H.P. equal to 0.4M for copper and 0.2M and 0.4M for cobalt the apparent value of $1/K_C$ is negative. The possibility of this happening has already been discussed on page 97.

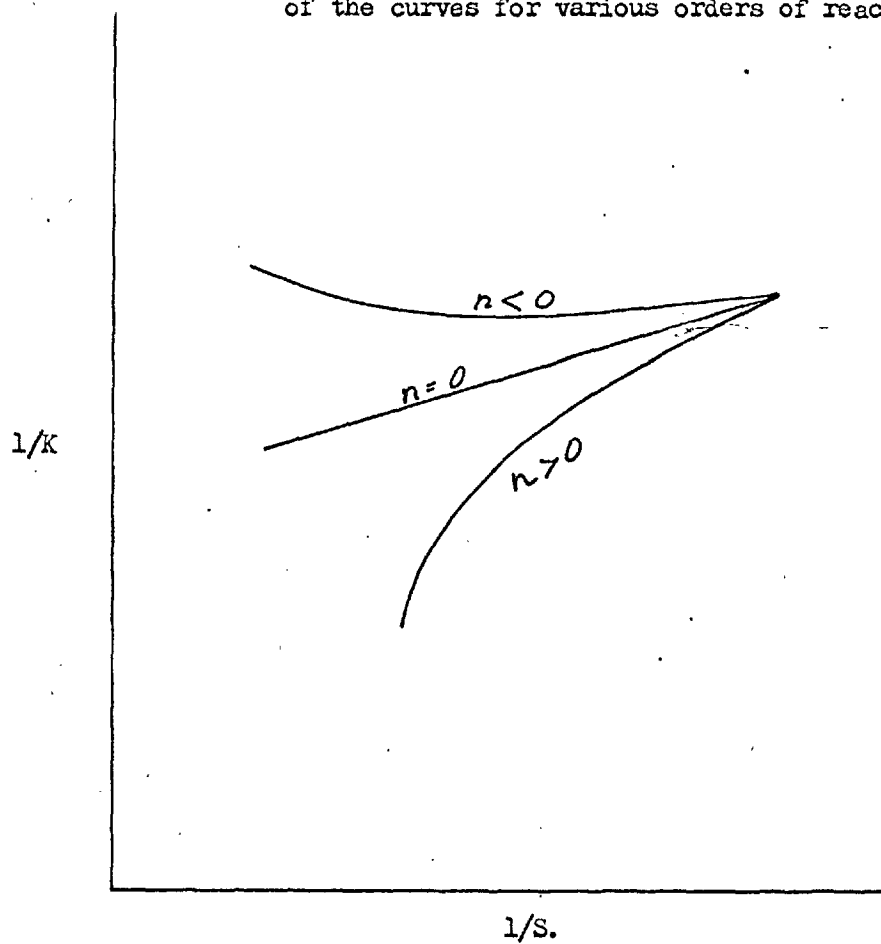
At concentrations of D.E.H.P. of 0.1M and below, the value of $1/K_C$ becomes significant for all three metals and the values found which are significant show no definite trend of variation, although there is a rather high random scatter on the results. Sufficient evidence is available, however, to show that $1/K_C$ cannot be proportional to D.E.H.P. concentration to a first or higher power since, if this were the case, the value of $1/K_C$ at high D.E.H.P. concentrations would be sufficiently great to be significant. However, the results do not preclude the possibility that $1/K_C$ is inversely proportional to D.E.H.P. concentration to a first or higher power.

(c) The influence of pH

The results and graphs for these runs are shown in Tables XXV-XXVII and XXXVI and Figures XXI-XXIII. The results of these runs follow an opposite pattern to those shown by D.E.H.P., i.e. increasing hydrogen ion concentration reduces the value of $1/b$. The variation of $1/b$ once again shows the same trend as that predicted theoretically and only at high values of pH is the value of $1/K_C$ statistically significant. The statistically significant values of $1/K_C$ do not show any definite trend of variation, but again there is considerable scatter in the results. By a similar argument to that used for variation of D.E.H.P. it is concluded that it is not possible for $1/K_C$ to be inversely proportional to the hydrogen ion concentration to a first or higher power, although a straight proportionality is possible. The results at high pH and low D.E.H.P. concentrations also lend extra weight to the finding that $1/K_C$ is independent of metal complex concentration. During runs at these concentration levels, the changes in $(C_S - C_W/m)$ are considerable (in some cases up to 40% of the metal being extracted by the end of each run). If $1/K_C$ is proportional to $(C_S - C_W/m)^n$, then the relationship between $1/K$ and $1/S$ would cease to be linear and would follow the trends shown in Fig. XXXV. Some small variation from linearity is to be expected due to the variation in $1/b$ with metal concentration. However, at high pH and low D.E.H.P. concentrations the values of $1/b$ are not statistically significant.

FIG XXXV

Graphs of $1/K$ versus $1/S$, showing the shape of the curves for various orders of reaction.



No consistent deviation from linearity can be observed as would be expected if n were greater than or less than 0. Although the evidence is not conclusive, a tentative relationship between $1/K_C$ and the three variables studied can be given as

$$1/K_C = [C_S - C_W/m]^0 [H^+]^0 + P[HR]^{0-q}$$

181.

where p and q are ≥ 0 .

The evidence in the case of cobalt is the least conclusive because of the lesser number of statistically significant values of $1/K_C$. This is a direct consequence of the larger diffusional resistances of the cobalt complex.

(d) The influence of temperature

The results and graphs for these runs are shown in Tables XXVIII-XXX and XXXVII and Figures XXIV-XXVI.

The variation of $1/b$ with temperature is not sufficient, when compared with the accuracy of the values, to give an accurate measure of the activation energy. However, this activation energy must be small, as is to be expected for diffusional resistance. Little can be said of the variation of $1/K_C$ with temperature, since only in the case of nickel were statistically significant figures obtained, and even here the level of significance was low. As examination of the graphs does not show large variations in $1/K_C$, a high value of activation energy is not likely.

(e) The influence of capryl alcohol

The results and graphs for these runs are shown in Tables XXXI-XXXIII and XXXVIII and Figure XXVII. Values of $1/b$ and $1/K_C$, in the absence of capryl alcohol, are given, in Table XXXVIII, for comparison. With all three metals the values of $1/K_C$ were found to be statistically insignificant and were apparently negative for copper and cobalt. Runs for all three metals at similar values of D.E.H.P. concentration, and pH, capryl alcohol absent, showed significant values of $1/K_C$ although in the case of copper the significance level was low. However, it would appear that the evidence is sufficient to show that there is a significant reduction in the value of $1/K_C$ in the presence of capryl alcohol.

4.2.3 Mechanism of Interfacial Resistance

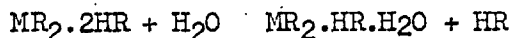
In this section a tentative mechanism, based on the phenomena of steric hindrance, will be put forward for the interfacial resistance. This mechanism is based on the following experimental evidence:-

- (i) The organic-metallic complex contains both organo-phosphate anions and neutral organo-phosphoric acid molecules in its structure.
- (ii) The rate of interfacial reaction is proportional to the driving force $(C_s - C_w/m)$, i.e. the interfacial resistance $1/K_c$ is independent of the driving force.
- (iii) The rate of the interfacial reaction increases in the presence of capryl alcohol which replaces the neutral D.E.H.P. molecules in the metal complex structure.
- (iv) The activation energy for the interfacial reaction is small.
- (v) Both D.E.H.P. and some organo-metallic species are adsorbed at the oil-water interface. This has been clearly shown in the interfacial tension measurements.

The hypothesis to be put forward assumes an organo-metallic complex of the form $MR_2 \cdot 2HR$. (Experimental evidence in the case of copper and nickel shows the form $MR_2 \cdot 3HR$. However on theoretical grounds the former has been shown to be more likely, although the argument to be put forward is applicable in either case.) Since each R group has two branched hydrocarbon chains the metal complex has eight branched chains radiating from the central metal atom; such a molecule will be spherical and rigid. It is unlikely that it will be adsorbed in the oil-water interface because it has a completely non-polar shell.

Some metal species is adsorbed, however, and this could be a molecule such as $MR_2 \cdot HR \cdot H_2O$, which is part way to the final species transferred to the aqueous solution.

The reaction is then:-



The removal of HR is more likely than R^- because it is less strongly held. This new molecule is nearer to hemispherical in

shape and the 'flat' face containing the $M-H_2O$ group is polar; hence, it can anchor the molecule to the aqueous phase. Thus adsorption is possible. Stripping of the remaining HR and R^- groups by H_2O and H^+ is relatively simple.

This first stage of the overall reaction is likely to be slow for steric reasons - the H_2O must penetrate into the paraffin phase and through the shell of the metal complex for reaction to occur.

The influences of pH and $D.E.H.P.$ concentration on the interfacial resistance have not been sufficiently well evaluated to tell whether they provide supporting evidence. However, the presence of capryl alcohol changes the structure of the molecule in such a way as to reduce the number of hydrocarbon chains radiating from the central metal atoms from eight to six. This will reduce the steric hindrance to penetration and hence reduce the interfacial resistance. This has been found to occur.

It is well known that the branching of the hydrocarbon groups has a marked influence on the properties of the organo-metallic complex, including the kinetics of reaction. This is more likely to arise from steric hindrance than some chemical shift.

4.3 CONCLUSIONS

For the cell described, the mass transfer of 8-hydroxyquinoline (Ox) was governed by the following relationship:-

$$\text{Rate} = [Ox] A(a_0 + b_0 S) \exp(-E/RT) \quad 182.$$

The rate was independent of the position of the area A across the cell and E was approximately 3.5 Kcal/mol. At stirring speeds above 50 r.p.m. this equation could be simplified to

$$\text{Rate} = [Ox] A(b^1 S) \exp(-E/RT) \quad 183.$$

The rate of stripping of metal-organophosphate complexes was studied using the equation:

$$1/K = 1/bS + 1/K_c \quad 184.$$

and it was found that the relative significance of $1/b$ and $1/K_c$ was dependent on the $D.E.H.P.$ and pH levels.

The evidence for a relationship between $1/K_c$, pH and $D.E.H.P.$ was not conclusive in view of the limited ranges of both variables over which $1/K_c$ was statistically significant.

To increase the range of $1/K_c$ significance by lowering the value of the diffusional resistance would have necessitated using higher stirring rates. With the cell design used this was not possible, as increase of stirring speed above 120 r.p.m. caused the interface to become unstable.

In the presence of capryl alcohol there is a significant lowering in the value of $1/K_c$.

From these experimental results, a tentative suggestion has been made that the rate determining step of the mechanism is the replacement of some of the neutral organo-phosphate molecules by water to allow adsorption of the molecule into the interface and that this step is accompanied by steric hindrance.

APPENDIX I.Calibrations for Spectrophotometric Analysis(a) 8-hydroxyquinoline (oxine)

The experimental technique used has been described in Section 2.4.1. The calibration is given in Table A and the calibration graph Figure A. These are for a 1 cm optical cell (silica).

TABLE A.

Conc. of oxine $\times 10^5$ M.	Optical Density
5	0.093
10	0.188
20	0.375
30	0.560
40	0.750

(b) Copper

The calibration figures for the rubeanic acid analysis for copper are given in Table B below and the calibration graph in Figure B. The concentrations of copper quoted are on the basis of a 1 cc original sample before dilution.

TABLE B.

Conc. of copper $\times 10^3$ M.	Optical Density 4 cm cell
0.2	0.115
0.5	0.278
1.0	0.558
2.0	1.068
3.0	1.610

(c) Nickel

The calibration figures and graph are given in Table C and Figure C respectively for the quinoxaline-2,3-dithiol analysis for nickel. The figures are again on the basis of a 1 cc original sample.

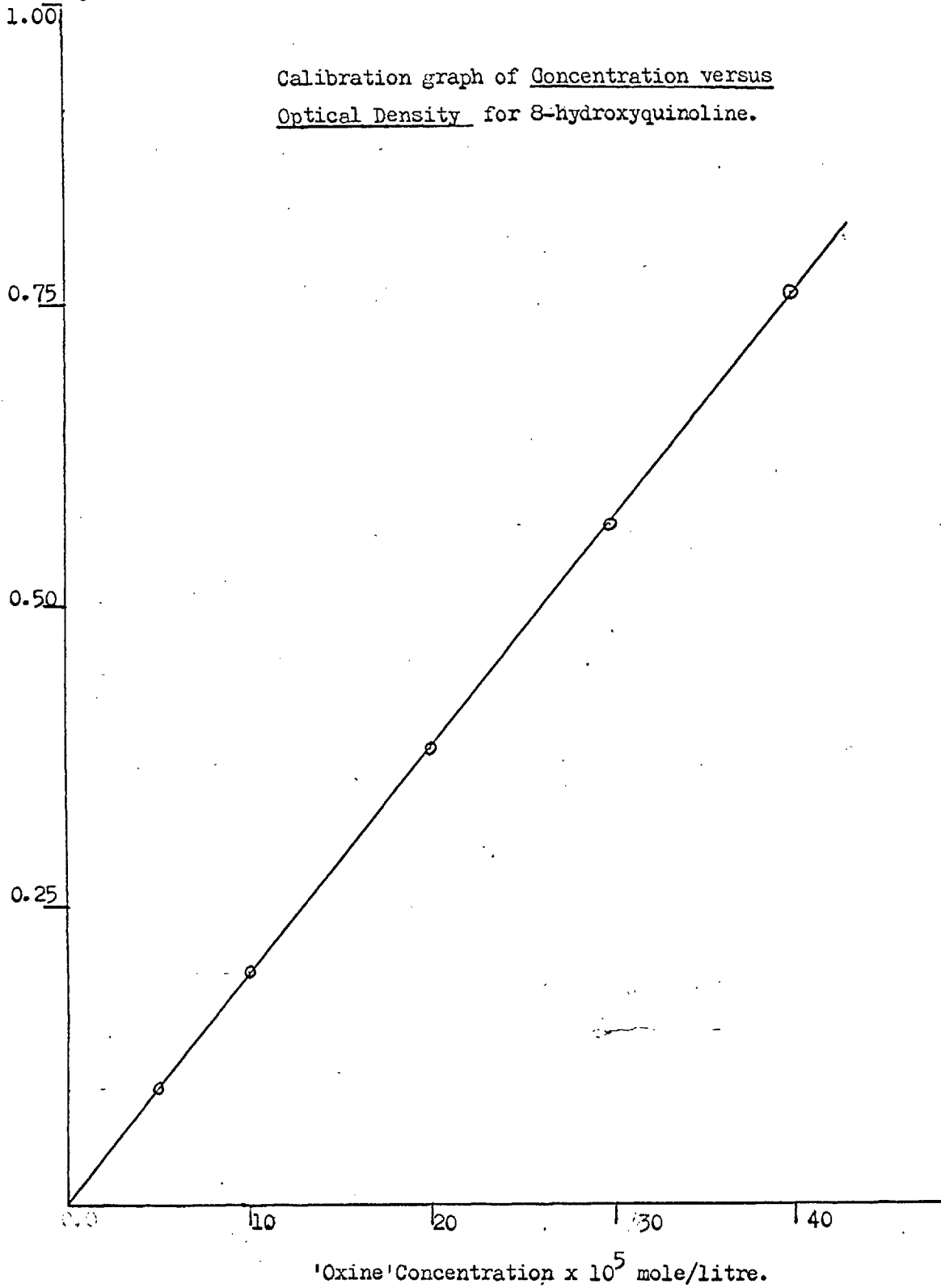
TABLE C.

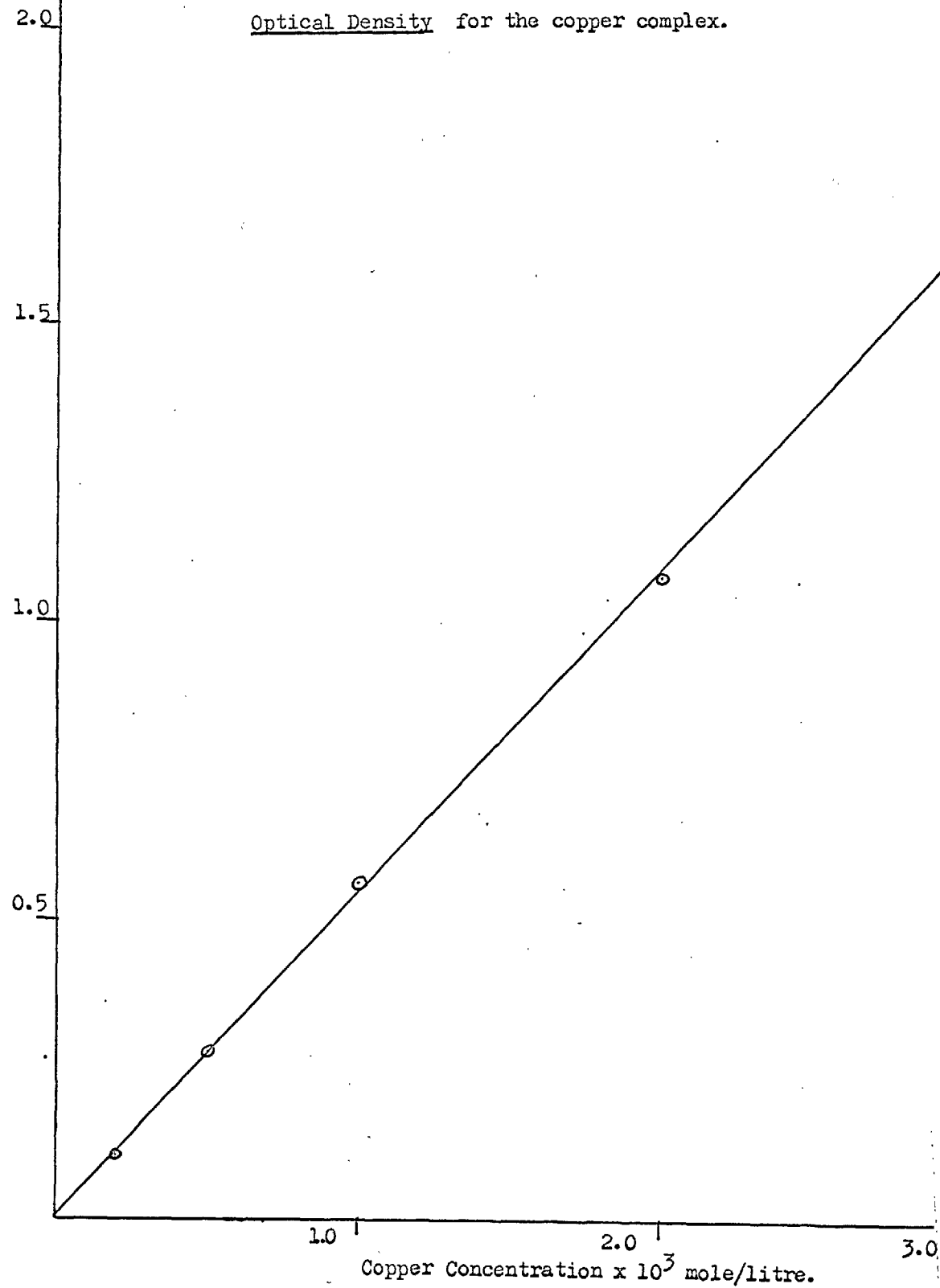
Conc. of nickel $\times 10^3$ M.	Optical Density 1 cm cell
0.1	0.088
0.2	0.172
0.5	0.432
1.0	0.868
2.0	1.750

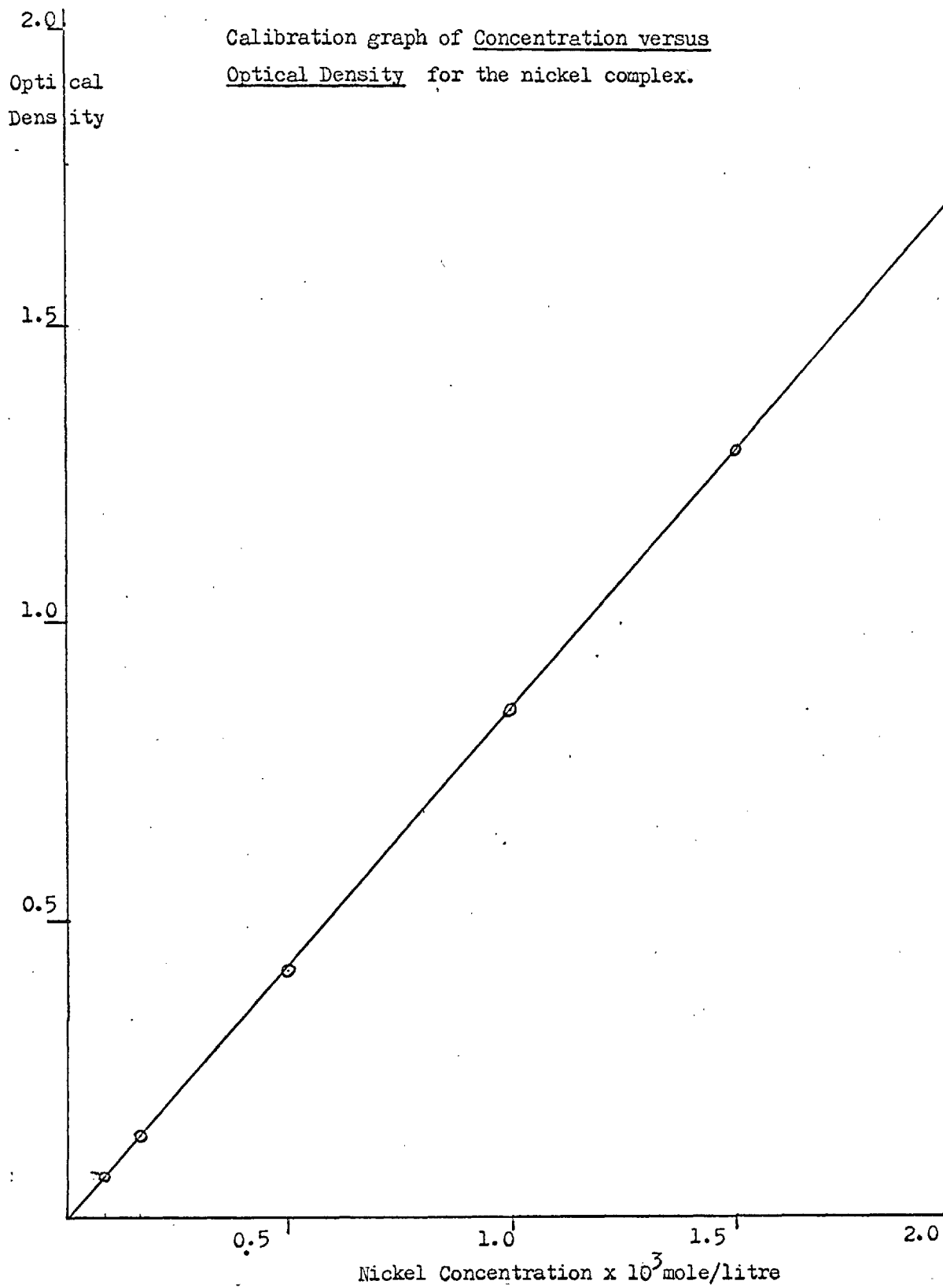
Optical
Density
1.00

APPENDIX FIG A

Calibration graph of Concentration versus
Optical Density for 8-hydroxyquinoline.



APPENDIX FIG BOptical
DensityCalibration graph of Concentration versus
Optical Density for the copper complex.

APPENDIX FIG C

APPENDIX II (a)

KINETIC RESULTS FOR THE TRANSFER OF 8-HYDROXYQUINOLINE INTO PARAFFIN

Time mins.	Organic Conc. C_s $\times 10^3$ mole/litre	Aqueous Conc. C_w $\times 10^3$ mole/litre	Log C_w	Time mins.	Organic Conc. C_s $\times 10^3$ mole/litre	Aqueous Conc. C_w $\times 10^3$ mole/litre	Log C_w
Ex No.1				Ex No.5			
0	0	1.88	-2.726	0	0	3.24	-2.490
30	0.070	1.80	-2.745	20	0.070	3.16	-2.501
60	0.185	1.67	-2.777	40	0.145	3.08	-2.512
90	0.285	1.56	-2.807	60	0.230	2.98	-2.526
120	0.350	1.49	-2.825	80	0.320	2.88	-2.541
150	0.405	1.42	-2.847	100	0.400	2.79	-2.555
180	0.490	1.33	-2.876	120	0.480	2.70	-2.569
220	0.555	1.26	-2.899	140	0.560	2.61	-2.584
246	0.600	1.20	-2.921				
270	0.640	1.16	-2.936				
300	0.690	1.10	-2.958				
330	0.745	1.04	-2.983				
Ex No.2				Ex No.6			
0	0	1.88	-2.726	0	0	3.24	-2.490
30	0.110	1.76	-2.755	20	0.120	3.10	-2.508
60	0.191	1.67	-2.772	40	0.210	3.00	-2.523
92	0.270	1.58	-2.801	62	0.340	2.86	-2.543
120	0.345	1.49	-2.827	80	0.445	2.74	-2.562
150	0.420	1.41	-2.851	100	0.545	2.63	-2.581
180	0.475	1.34	-2.873	120	0.630	2.53	-2.597
220	0.535	1.28	-2.892	140	0.715	2.43	-2.615
250	0.575	1.22	-2.914				
275	0.650	1.15	-2.939				
300	0.685	1.11	-2.955				
330	0.735	1.05	-2.979				
Ex No.4				Ex No.7			
0	0	0.82	-3.086	0	0	3.24	-2.490
21	0.065	0.75	-3.125	20	0.160	3.06	-2.514
42	0.085	0.72	-3.142	40	0.320	2.88	-2.541
60	0.105	0.70	-3.156	60	0.465	2.72	-2.565
80	0.120	0.68	-3.168	82	0.615	2.55	-2.593
100	0.140	0.66	-3.189	100	0.740	2.41	-2.617
123	0.160	0.64	-3.194	120	0.825	2.31	-2.637
140	0.190	0.61	-3.215	140	0.915	2.21	-2.656

Time mins.	Organic Conc. C_s $\times 10^3$ mole/litre	Aqueous Conc. C_w $\times 10^3$ mole/litre	Log C_w	Time mins.	Organic Conc. C_s $\times 10^3$ mole/litre	Aqueous Conc. C_w $\times 10^3$ mole/litre	Log C_w
Ex No. 8				Ex No. 21			
0	0	3.24	-2.490	0	0	3.24	-2.490
20	0.265	2.97	-2.527	5	0.120	3.10	-2.509
40	0.445	2.74	-2.562	10	0.255	2.95	-2.530
60	0.600	2.56	-2.592	15	0.445	2.74	-2.562
80	0.730	2.42	-2.617	20	0.550	2.62	-2.582
110	0.880	2.25	-2.648	25	0.640	2.52	-2.599
125	0.955	2.17	-2.664	30	0.765	2.38	-2.623
140	1.030	2.08	-2.692				
Ex No. 9				Ex No. 22			
0	0	3.24	-2.490	0	0	3.24	-2.490
22	0.165	3.05	-2.516	11	0.145	3.08	-2.511
40	0.320	2.88	-2.541	20	0.270	2.94	-2.532
63	0.470	2.71	-2.568	30	0.390	2.80	-2.553
81	0.610	2.55	-2.594	42.5	0.515	2.66	-2.575
104	0.755	2.38	-2.623	51	0.600	2.56	-2.592
123	0.865	2.27	-2.645	60	0.680	2.47	-2.607
140	0.960	2.16	-2.666				
Ex No. 10				Ex No. 23			
0	0	3.24	-2.490	0	0	3.24	-2.490
20	0.105	3.12	-2.506	5	0.200	3.01	-2.522
40	0.175	3.04	-2.517	10	0.380	2.81	-2.552
68	0.255	2.95	-2.530	15	0.555	2.61	-2.584
86	0.300	2.90	-2.538	20	0.710	2.44	-2.613
105	0.350	2.85	-2.546	25	0.845	2.29	-2.640
122	0.390	2.80	-2.553	30	0.970	2.15	-2.668
140	0.435	2.75	-2.561				
Ex No. 11				Ex No. 62			
0	0	3.24	-2.490	0	0.045	2.95	-2.530
20	0.140	3.08	-2.511	5	0.195	2.80	-2.553
44	0.195	3.02	-2.520	10	0.355	2.64	-2.578
64	0.240	2.97	-2.528	15	0.480	2.52	-2.599
82	0.320	2.88	-2.541	20	0.605	2.39	-2.622
103	0.380	2.82	-2.550	25	0.750	2.25	-2.648
126	0.420	2.78	-2.557				
140	0.450	2.73	-2.564				
Ex No. 12				Ex No. 63			
0	0	3.24	-2.490	0	0.050	2.94	-2.532
20	0.165	3.05	-2.516	5	0.270	2.73	-2.564
40	0.255	2.95	-2.531	10.5	0.465	2.53	-2.597
60	0.350	2.84	-2.547	15	0.640	2.36	-2.628
80	0.440	2.74	-2.562	20	0.810	2.19	-2.660
102	0.535	2.64	-2.578	25	0.965	2.03	-2.693
120	0.620	2.54	-2.594				
140	0.705	2.45	-2.611				

Time mins.	Organic Conc. C_s $\times 10^3$ mole/litre	Aqueous Conc. C_w $\times 10^3$ mole/litre	Log C_w	Time mins.	Organic Conc. C_s $\times 10^3$ mole/litre	Aqueous Conc. C_w $\times 10^3$ mole/litre	Log C_w
Ex No.64				Ex No.70			
0	0.045	2.95	-2.530	0	0.485	2.51	-2.599
5	0.140	2.86	-2.544	5	0.655	2.34	-2.630
10	0.215	2.78	-2.556	10	0.810	2.19	-2.660
15.2	0.290	2.71	-2.570	15	0.945	2.05	-2.687
20	0.360	2.64	-2.579	20	1.070	1.93	-2.715
25	0.445	2.55	-2.593	25.5	1.200	1.80	-2.745
Ex No.65				Ex No.71			
0	0.055	2.94	-2.531	0	0.055	2.94	-2.531
5.3	0.260	2.74	-2.562	6	0.200	2.80	-2.553
10	0.425	2.57	-2.590	10	0.300	2.70	-2.569
15	0.590	2.41	-2.618	15	0.425	2.57	-2.590
20	0.740	2.26	-2.646	21	0.550	2.45	-2.611
25	0.835	2.11	-2.676	25	0.640	2.36	-2.628
Ex No.66				Ex No.72			
0	0.050	2.95	-2.530	a) 0	0.040	2.96	-2.529
5	0.175	2.82	-2.549	5.5	0.105	2.89	-2.538
10	0.270	2.73	-2.564	10	0.165	2.83	-2.547
15	0.380	2.62	-2.582	17	0.270	2.73	-2.564
20	0.485	2.52	-2.598	21	0.340	2.66	-2.575
25	0.570	2.43	-2.614	25	0.415	2.58	-2.587
Ex No.67				b) 0			
0	0.080	2.92	-2.535	5.1	0.500	2.50	-2.602
5	0.240	2.76	-2.559	10.2	0.605	2.39	-2.621
10.5	0.405	2.59	-2.566	15.0	0.700	2.30	-2.638
15	0.530	2.47	-2.603	21.5	0.785	2.21	-2.656
21	0.645	2.35	-2.628	25	0.865	2.13	-2.671
25	0.730	2.27	-2.644	25	0.920	2.08	-2.682
Ex No.68				c) 0			
0	0.055	2.94	-2.531	5.5	1.025	1.97	-2.705
10	0.175	2.82	-2.550	10	1.130	1.87	-2.728
20	0.305	2.69	-2.569	15	1.190	1.81	-2.742
30	0.410	2.59	-2.587	15	1.265	1.73	-2.762
40.2	0.540	2.46	-2.609	20	1.340	1.66	-2.780
51.1	0.655	2.38	-2.622	25	1.420	1.58	-2.801
Ex No.69				Ex No.73			
0	0.055	2.94	-2.531	a) 0	0.035	2.96	-2.529
5	0.135	2.86	-2.543	6	0.240	2.76	-2.559
10	0.200	2.80	-2.553	10.2	0.385	2.61	-2.583
15	0.270	2.73	-2.564	15	0.550	2.45	-2.611
20.1	0.340	2.66	-2.575	20	0.705	2.29	-2.639
26	0.420	2.58	-2.588	25.0	0.815	2.18	-2.660
				b) 0			
				5	0.975	2.02	-2.693
				10	1.100	1.90	-2.722
				15.5	1.240	1.76	-2.754
				20	1.365	1.63	-2.787
				20	1.450	1.55	-2.810
				25	1.560	1.44	-2.842

APPENDIX II (b)

KINETIC RESULTS FOR THE STRIPPING OF COPPER FROM D.E.H.P.

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_w x 10^3 mole/litre	Organic Conc. C_s x 10^3 mole/litre (mean)	Stirrer Speed r.p.m.	Aqueous Conc. C_w x 10^3 mole/litre	Organic Conc. C_s x 10^3 mole/litre (mean)
	Ex No.49			Ex No.51		
0	27	0.004		27	0.061	
5	27	0.052		27	0.133	
10	27	0.101	8.48	27	0.186	12.45
15	27	0.189		27	0.263	
20	27/50	0.206		27/51	0.324	
25	50	0.275		51	0.414	
30	50	0.383	8.47	51	0.526	12.10
35	50	0.445		51	0.613	
40	50/74	0.506		51/74	0.700	
45	74	0.669		74	0.850	
50	74	0.758	8.09	74	0.952	11.67
55	74	0.856		74	1.148	
60	74/98	0.948		74/98	1.276	
65	98	1.064		98	1.380	
70	98	1.198	7.60	98	1.512	11.09
75	98	1.324		98	1.630	
80	98/122	1.452		98/122	1.800	
85	122	1.568		122	1.893	
90	122	1.697	7.15	122	2.040	10.53
95	122	1.819		122	2.158	
100	122	1.930		122	2.292	
	Ex No.50			Ex No.52		
0	51	0.079		27	0.016	
5	51	0.174		27	0.043	
10	51	0.285	17.12	27	0.068	3.81
15	51	0.583		27	0.088	
20	51/27	0.609		27/51	0.114	
25	27	0.699		51	0.144	
30	27	0.756	16.64	51	0.180	3.70
35	27	0.854		51	0.212	
40	27/74	0.942		51/74	0.243	
45	74	1.139		74	0.293	
50	74	1.339	16.04	74	0.340	3.53
55	74	1.461		74	0.390	
60	74/98	1.662		74/98	0.429	
65	98	1.882		98	0.478	
70	98	2.145	15.21	98	0.533	3.33
75	98	2.372		98	0.560	
80	98/121	2.538		98/122	0.624	
85	121	2.771		122	0.671	
90	121	3.021	14.28	122	0.719	3.14
95	121	3.205		122	0.757	
100	121	3.397		122	0.826	

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_w x 10^3 mole/litre	Organic Conc. C_s x 10^3 mole/litre (mean)	Stirrer Speed r.p.m.	Aqueous Conc. C_w x 10^3 mole/litre	Organic Conc. C_s x 10^3 mole/litre (mean)
	Ex No.53			Ex No.55		
0	27	0.034		28	0.137	
5	27	0.066		28	0.279	
10	27	0.102	7.25	26	0.415	6.74
15	27	0.124		28	0.531	
20	27/51	0.150		28/52	0.704	
25	51	0.204		52	0.858	
30	51	0.245	7.10	52	1.032	6.12
35	51	0.299		52	1.175	
40	51/75	0.336		52/74	1.282	
45	75	0.415		74	1.368	
50	75	0.488	6.85	74	1.534	5.60
55	75	0.544		74	1.636	
60	75/98	0.582		74/98	1.806	
65	98	0.645		98	1.881	
70	98	0.734	6.64	98	2.063	5.04
75	98	0.800		98	2.119	
80	98/122	0.840		98/123	2.325	
85	122	0.917		123	2.459	
90	122	0.965	6.35	123	2.570	4.50
95	122	1.019		123	2.704	
100	122	1.091		123	2.773	
	Ex No.54			Ex No.56		
0	27	0.082		28	0.125	
5	27	0.186		28	0.286	
10	27	0.272	7.05	28	0.421	6.57
15	27	0.368		28	0.589	
20	27/51	0.468		28/51	0.712	
25	51	0.604		51	0.886	
30	51	0.765	6.55	51	1.059	5.92
35	51	0.851		51	1.268	
40	51/74	0.966		51/74	1.378	
45	74	1.109		74	1.546	
50	74	1.285	6.01	74	1.632	5.33
55	74	1.407		74	1.933	
60	74/98	1.592		74/99	2.026	
65	98	1.744		99	2.200	
70	98	1.905	5.36	99	2.352	4.58
75	98	2.034		99	2.509	
80	98/122	2.159		99/123	2.643	
85	122	2.293		123	2.788	
90	122	2.410	4.82	123	2.924	3.97
95	122	2.549		123	3.081	
100	122	2.664		123	3.207	

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_w $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre (mean)	Stirrer Speed r.p.m.	Aqueous Conc. C_w $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre (mean)
	Ex.No.57			Ex No.59		
0	27	0.027		26	0.141	
5	27	0.081		26	0.231	
10	27	0.133	8.77	26	0.501	8.40
15	27	0.181		26	0.671	
20	27/51	0.238		26/49	0.893	
25	51	0.303		49	1.135	
30	51	0.362	8.53	50	1.375	7.51
35	51	0.438		50	1.584	
40	51/75	0.491		50/75	1.699	
45	75	0.565		75	1.935	
50	75	0.683	8.20	75	2.155	6.70
55	75	0.740		75	2.397	
60	75/99	0.822		75/99	2.594	
65	99	0.903		99	2.800	
70	99	1.005	7.87	99	3.033	5.78
75	99	1.119		99	3.210	
80	99/123	1.194		99/123	3.382	
85	123	1.303		123	3.507	
90	123	1.411	7.46	123	3.790	4.97
95	123	1.518		123	3.928	
100	123	1.624		123	4.098	
	Ex No.58			Ex No.60		
0	26	0.036		26	0.193	
5	26	0.104		26	0.438	
10	26	0.161	8.74	26	0.709	8.19
15	26	0.224		26	1.003	
20	26/50	0.303		26/49	1.316	
25	50	0.380		49	1.504	
30	50	0.500	8.39	49	1.834	7.05
35	50	0.600		49	2.019	
40	50/75	0.717		49/74	2.371	
45	75	0.857		74	2.615	
50	75	0.951	7.93	74	2.855	5.98
55	75	1.139		74	3.088	
60	75/99	1.293		74/99	3.292	
65	99	1.451		99	3.483	
70	99	1.651	7.21	99	3.673	5.13
75	99	1.776		99	3.859	
80	99/123	1.932		99/124	4.027	
85	123	2.082		124	4.201	
90	123	2.231	6.59	124	4.360	4.38
95	123	2.421		124	4.513	
100	123	2.535		124	4.671	

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_w $\times 10^3$ mole/litre	Organic Conc. C_o $\times 10^3$ mole/litre (mean)	Stirrer Speed r.p.m.	Aqueous Conc. C_w $\times 10^3$ mole/litre	Organic Conc. C_o $\times 10^3$ mole/litre (mean)
	Ex No. 88			Ex No. 93		
0	22	0.124		36	0.172	
5	22	0.175		36	0.297	
10	22	0.254	8.65	36	0.358	8.54
15	22	0.328		35	0.534	
20	22/48	0.408		37/52	0.619	
25	49	0.500		52	0.759	
30	49	0.578	8.31	52	0.865	8.03
35	49	0.636		52	1.070	
40	49/73	0.769		52/78	1.280	
45	73	0.850		78	1.368	
50	73	0.993	7.89	77	1.629	7.24
55	73	1.102		78	1.700	
60	73/100	1.259		77/104	2.023	
65	100	1.378		104	2.184	
70	100	1.539	7.32	104	2.349	6.47
75	100	1.704		103	2.565	
80	100/125	1.817		103/129	2.802	
85	125	1.984		129	3.024	
90	125	2.177	6.65	129	3.296	5.49
95	125	2.327		129	3.516	
100	125	2.416		129	3.744	
	Ex No. 92			Ex No. 94		
0	26	0.048		38	0.111	
5	26	0.170		37	0.220	
10	26	0.245	8.65	37	0.344	8.56
15	26	0.311		36	0.485	
20	26/49	0.403		37/52	0.545	
25	49	0.528		51	0.686	
30	49	0.655	8.24	52	0.920	7.97
35	49	0.780		52	1.050	
40	49/73	0.931		52/77	1.230	
45	74	1.101		77	1.375	
50	74	1.262	7.61	77	1.597	7.27
55	73	1.464		78	1.797	
60	73/100	1.632		77/104	1.874	
65	101	1.848		104	2.074	
70	101	2.085	6.76	104	2.315	6.52
75	100	2.225		103	2.570	
80	100/126	2.479		103/129	2.813	
85	126	2.633		130	2.959	
90	126	2.923	5.87	129	3.079	5.72
95	126	3.132		130	3.258	
100	126	3.334		130	3.683	

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_w $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre (mean)
	Ex No. 96		
0	38	0.208	
5	38	0.258	
10	37	0.329	7.69
15	38	0.426	
20	37/51	0.483	
25	52	0.612	
30	52	0.741	7.27
35	52	0.816	
40	52/78	0.877	
45	78	1.041	
50	78	1.135	6.86
55	78	1.271	
60	78/103	1.415	
65	103	1.722	
70	103	1.855	6.11
75	103	1.969	
80	103/129	2.095	
85	129	2.363	
90	129	2.557	5.38
95	129	2.761	
100	129	2.961	

APPENDIX II (c)

KINETIC RESULTS FOR THE STRIPPING OF COBALT FROM D.E.H.P.

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_a x 10^3 mole/litre	Organic Conc. C_s x 10^3 mole/litre	Stirrer Speed r.p.m.	Aqueous Conc. C_a x 10^3 mole/litre	Organic Conc. C_s x 10^3 mole/litre
	Ex No.75			Ex No.77		
0	31	0.147		30	0.047	
5	31	0.219		30	0.071	
10	31	0.308	6.33	30	0.084	6.56
15	31	0.435		30	0.101	
20	31/52	0.542		30/52	0.133	
25	52	0.685		52	0.171	
30	52	0.839	5.79	52	0.215	6.41
35	52	1.049		52	0.240	
40	52/77	1.163		52/78	0.278	
45	77	1.325		78	0.341	
50	77	1.533	5.08	78	0.391	6.24
55	77	1.655		78	0.496	
60	77/103	1.756		78/104	0.564	
65	103	1.936		104	0.676	
70	103	2.039	4.55	104	0.740	5.83
75	103	2.189		104	0.833	
80	103/130	2.330		104/130	0.961	
85	130	2.455		130	1.057	
90	130	2.604	3.94	130	1.142	5.46
95	130	2.729		130	1.239	
100	130	2.855		130	1.431	
	Ex No.76			Ex No.78		
0	31	0.072		29	0.105	
5	31	0.105		30	0.203	
10	31	0.159	6.48	35	0.401	6.24
15	31	0.184		30	0.578	
20	31/52	0.211		29/51	0.684	
25	52	0.293		53	0.796	
30	52	0.369	6.27	53	0.866	5.76
35	52	0.417		53	1.028	
40	51/78	0.596		53/79	1.134	
45	78	0.669		79	1.242	
50	78	0.796	5.83	79	1.366	5.25
55	78	0.939		79	1.496	
60	78/104	1.040		79/105	1.603	
65	104	1.205		105	1.661	
70	104	1.328	5.27	103	1.730	4.86
75	104	1.397		104	1.812	
80	104/130	1.605		105/130	2.010	
85	130	1.734		130	2.148	
90	130	1.828	4.75	130	2.217	4.35
95	130	1.923		130	2.346	
100	130	2.105		130	2.450	

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_a x 10^3 mole/litre	Organic Conc. C_s x 10^3 mole/litre	Stirrer Speed r.p.m.	Aqueous Conc. C_a x 10^3 mole/litre	Organic Conc. C_s x 10^3 mole/litre
	Ex No.79			Ex No.81		
0	25	0.128		27	0.034	
5	25	0.160		26	0.055	
10	26	0.187	13.96	26	0.081	3.46
15	26	0.234		27	0.105	
20	26/50	0.301		27/52	0.130	
25	52	0.426		52	0.151	
30	52	0.589	13.55	52	0.189	3.35
35	52	0.664		51	0.237	
40	52/78	0.767		51/78	0.286	
45	78	0.965		78	0.354	
50	78	1.068	13.06	78	0.426	3.11
55	78	1.271		78	0.488	
60	78/104	1.479		78/104	0.553	
65	104	1.663		104	0.620	
70	104	1.921	12.18	104	0.696	2.82
75	104	2.186		104	0.767	
80	104/130	2.366		104/130	0.827	
85	130	2.645		130	0.900	
90	130	2.864	11.18	130	0.950	2.56
95	130	3.072		130	1.033	
100	130	3.280		130	1.082	
	Ex No.80			Ex No.82		
0	26	0.045		26	0.028	
5	26	0.075		29	0.037	
10	27	0.102	9.30	30	0.049	6.59
15	27	0.143		30	0.066	
20	27/51	0.199		29/51	0.072	
25	51	0.293		52	0.117	
30	50	0.375	9.02	52	0.146	6.49
35	50	0.479		52	0.188	
40	50/77	0.559		52/78	0.237	
45	77	0.636		78	0.273	
50	77	0.792	8.59	78	0.319	6.31
55	77	0.879		78	0.352	
60	77/104	1.000		78/105	0.425	
65	104	1.168		105	0.499	
70	104	1.346	8.02	105	0.572	6.05
75	104	1.509		105	0.604	
80	104/130	1.661		105/131	0.685	
85	130	1.785		131	0.756	
90	130	1.955	7.37	130	0.822	5.79
95	130	2.160		130	0.900	
100	130	2.334		130	0.958	

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_a $\times 10^3$ mole/litre	Organic Conc. C_G $\times 10^3$ mole/litre	Stirrer Speed r.p.m.	Aqueous Conc. C_a $\times 10^3$ mole/litre	Organic Conc. C_G $\times 10^3$ mole/litre
Ex No.83				Ex No.85		
0	25	0.014		30	0.038	
5	29	0.031		27	0.075	
10	29	0.050	6.39	27	0.103	7.21
15	29	0.074		27	0.162	
20	29/51	0.104		27/52	0.225	
25	52	0.153		53	0.307	
30	52	0.209	6.23	53	0.425	6.89
35	52	0.268		52	0.476	
40	52/78	0.315		52/79	0.615	
45	79	0.399		79	0.759	
50	79	0.432	6.00	79	0.951	6.34
55	78	0.575		79	1.130	
60	78/105	0.648		79/105	1.309	
65	105	0.785		104	1.543	
70	105	0.890	5.52	104	1.734	5.54
75	105	1.002		104	1.953	
80	105/130	1.102		104/130	2.158	
85	130	1.238		130	2.421	
90	130	1.403	4.99	130	2.704	4.52
95	130	1.495		130	2.947	
100	130	1.632		130	3.221	
Ex No.84				Ex No.86		
0	29	0.037		29	0.042	
5	26	0.064		27	0.060	
10	27	0.082	4.40	27	0.094	6.55
15	27	0.109		29	0.120	
20	26/49	0.136		30/52	0.155	
25	53	0.219		53	0.222	
30	53	0.294	4.18	52	0.300	6.34
35	51	0.373		52	0.377	
40	48/78	0.451		49/78	0.453	
45	78	0.570		79	0.536	
50	78	0.682	3.78	78	0.680	5.95
55	78	0.795		79	0.825	
60	78/105	0.913		79/105	0.940	
65	105	1.037		105	1.071	
70	105	1.145	3.30	103	1.193	5.42
75	105	1.261		103	1.341	
80	105/130	1.371		105/130	1.491	
85	130	1.478		130	1.650	
90	130	1.587	2.84	130	1.751	4.83
95	130	1.691		130	1.863	
100	130	1.803		130	2.040	

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_a $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre	Stirrer Speed r.p.m.	Aqueous Conc. C_a $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre
	Ex No. 87			Ex No. 91		
0	25	0.021		25	0.025	
5	26	0.039		26	0.035	
10	26	0.055	6.58	26	0.055	6.58
15	26	0.081		27	0.088	
20	26/49	0.102		27/49	0.113	
25	49	0.135		49	0.162	
30	49	0.172	6.49	49	0.207	6.43
35	49	0.223		49	0.244	
40	49/74	0.262		49/73	0.315	
45	73	0.316		73	0.370	
50	74	0.385	6.25	73	0.463	6.17
55	74	0.472		73	0.538	
60	74/100	0.553		73/100	0.551	
65	99	0.694		100	0.649	
70	99	0.754	5.86	100	0.787	5.83
75	99	0.842		101	0.844	
80	99/125	0.912		101/126	0.961	
85	125	1.001		126	1.118	
90	125	1.096	5.51	126	1.221	5.38
95	125	1.202		126	1.384	
100	125	1.300		126	1.570	

APPENDIX II (d)

KINETIC RESULTS FOR THE STRIPPING OF NICKEL FROM D.E.H.P.

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_a $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre	Stirrer Speed r.p.m.	Aqueous Conc. C_a $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre
	Ex No.89			Ex No.99		
0	25	0.144		29	0.103	
5	25	0.181		31	0.174	
10	25	0.217	6.22	31	0.254	6.19
15	25	0.254		31	0.347	
20	25/49	0.292		31/51	0.440	
25	49	0.358		52	0.589	
30	49	0.457	5.98	52	0.717	5.71
35	49	0.526		52	0.824	
40	49/73	0.591		52/77	0.941	
45	73	0.682		77	1.035	
50	73	0.773	5.65	77	1.202	5.21
55	73	0.830		77	1.340	
60	73/100	0.948		77/103	1.469	
65	99	1.040		103	1.603	
70	99	1.167	5.24	103	1.760	4.63
75	99	1.280		103	1.863	
80	99/125	1.373		103/130	2.014	
85	125	1.492		130	2.155	
90	125	1.592	4.79	130	2.286	4.07
95	125	1.728		130	2.400	
100	125	1.846		130	2.522	
	Ex No.90			Ex No.99		
0	25	0.201		34	0.118	
5	26	0.242		34	0.191	
10	26	0.295	6.14	35	0.268	6.17
15	26	0.353		35	0.358	
20	26/49	0.413		34/51	0.435	
25	49	0.509		52	0.546	
30	49	0.605	5.83	52	0.661	5.76
35	49	0.683		52	0.769	
40	49/73	0.767		52/77	0.869	
45	73	0.833		77	1.016	
50	74	0.983	5.44	77	1.151	5.26
55	74	1.036		77	1.277	
60	73/100	1.194		77/103	1.453	
65	100	1.311		103	1.587	
70	100	1.431	4.97	103	1.718	4.68
75	100	1.566		103	1.850	
80	100/125	1.652		103/129	1.991	
85	125	1.733		129	2.075	
90	125	1.837	4.49	129	2.222	4.14
95	125	2.024		129	2.350	
100	125	2.179		129	2.500	

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_a $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre	Stirrer Speed r.p.m.	Aqueous Conc. C_a $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre
Ex No. 100				Ex No. 102		
0	30	0.041		30	0.217	
5	30	0.061		31	0.370	
10	30	0.085	6.35	31	0.529	5.91
15	30	0.108		31	0.688	
20	30/51	0.138		31/51	0.835	
25	51	0.186		51	1.031	
30	51	0.227	6.21	51	1.233	5.19
35	51	0.268		51	1.392	
40	51/77	0.316		51/77	1.525	
45	77	0.367		77	1.669	
50	77	0.424	6.01	77	1.803	4.60
55	77	0.475		77	1.953	
60	77/103	0.543		77/103	2.085	
65	103	0.600		103	2.187	
70	103	0.660	5.76	103	2.305	4.06
75	103	0.732		103	2.443	
80	103/129	0.791		103/129	2.565	
85	129	0.867		129	2.683	
90	129	0.953	5.45	129	2.784	3.56
95	129	1.030		129	2.904	
100	129	1.100		129	3.003	
Ex No. 101				Ex No. 103		
0	31	0.073		34	0.312	
5	34	0.137		34	0.453	
10	35	0.305	6.13	34	0.587	11.77
15	35	0.414		34	0.711	
20	35/53	0.520		34/52	0.783	
25	53	0.662		52	0.859	
30	53	0.790	5.64	52	1.001	11.35
35	53	0.919		52	1.100	
40	53/77	1.044		52/77	1.221	
45	77	1.200		77	1.351	
50	77	1.348	5.07	77	1.498	10.83
55	77	1.483		77	1.641	
60	77/103	1.601		77/103	1.771	
65	103	1.711		103	1.958	
70	103	1.848	4.54	103	2.200	10.10
75	103	1.950		103	2.396	
80	103/129	2.037		103/129	2.592	
85	129	2.154		129	2.814	
90	129	2.253	4.09	129	3.036	9.22
95	129	2.365		129	3.234	
100	129	2.473		129	3.465	

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_a $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre	Stirrer Speed r.p.m.	Aqueous Conc. C_a $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre
	Ex No. 104			Ex No. 105		
0	35	.128		47	0.070	
5	35	.235		50	0.116	
10	35	.323	10.08	52	0.150	6.49
15	35	.458		52	0.185	
20	35/52	.537		52/78	0.243	
25	52	.631		78	0.315	
30	52	.750	9.64	78	0.361	6.38
35	52	.849		78	0.423	
40	52/78	1.001		76/104	0.475	
45	78	1.144		104	0.550	
50	78	1.302	9.07	104	0.612	6.01
55	78	1.465		104	0.683	
60	78/103	1.630		104/130	0.752	
65	103	1.817		130	0.833	
70	103	2.013	8.33	130	0.883	5.73
75	103	2.200		130	0.942	
80	103/129	2.376		130	1.045	
85	129	2.581				
90	129	2.805	7.49			
95	129	2.979				
100	129	3.168				
	Ex No. 105			Ex No. 107		
0	35	0.053		48	0.120	
5	35	0.058		49	0.204	
10	35	0.025	4.72	49	0.284	3.59
15	35	0.134		49	0.369	
20	35/52	0.156		49/77	0.462	
25	52	0.245		79	0.599	
30	52	0.287	4.52	79	0.693	3.17
35	52	0.347		79	0.787	
40	52/78	0.408		79/104	0.868	
45	78	0.492		104	0.985	
50	78	0.567	4.23	104	1.089	2.76
55	78	0.648		104	1.153	
60	75/103	0.720		102/129	1.205	
65	103	0.807		129	1.267	
70	103	0.904	3.88	129	1.380	2.44
75	103	0.992		129	1.440	
80	103/129	1.090		129	1.555	
85	129	1.173				
90	129	1.266	3.52			
95	129	1.348				
100	129	1.445				

Time mins.	Stirrer Speed r.p.m.	Aqueous Conc. C_a $\times 10^3$ mole/litre	Organic Conc. C_s $\times 10^3$ mole/litre
Ex No. 103			
0	30	0.146	
5	30	0.207	
10	30	0.230	4.58
15	30	0.293	
20	30/52	0.305	
25	52	0.410	
30	52	0.474	4.33
35	52	0.596	
40	52/78	0.679	
45	78	0.801	
50	78	0.921	3.87
55	78	1.034	
60	78/103	1.150	
65	103	1.326	
70	104	1.439	3.33
75	104	1.540	
80	104/129	1.651	
85	129	1.784	
90	129	1.943	2.80
95	129	2.054	
100	129	2.186	

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