# The University of Liverpool <br> Faculty of Science <br> Department of Chemistry 

# Electrochemistry at Liquid/Liquid Interfaces for Metal Ion Extraction 

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# Abstract. <br> Electrochemistry at Liquid/Liquid Interfaces for Metal Ion Extraction 

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The aim of this project was to produce a selective extraction system for the separation of precious metal ions from waste electrolyte streams utilising liquid/liquid electrochemical techniques. During the course of this project the work partitioned into three different aspects of charge transfer: electron transfer, ion transfer and membrane studies.

Some fundamental physicochemical properties of liquid/liquid systems were explored. For electron transfer reactions the dependence of the rate of electron transfer on supporting electrolyte concentration in the organic phase for the water/1,2-DCE interface was measured using the technique of interfacial electrochemical impedance spectroscopy. No dependence of the rate of electron transfer on the concentration of the supporting electrolyte in the organic phase was observed. The effect of the solvent on the kinetics of electron transfer has also been examined. The results show that the rate does not follow the expected Marcusian dependence. Several solvents previously unused for liquid/liquid studies have been screened; one solvent in particular, 1,2-difluorobenzene, shows great promise for future work.

The ion transfer studies show that platinates can be separated under potential control across the water/1,2-DCE and the water/methyl isobutyl ketone interfaces. Ion transfer and separation of chloroaurate and chloroplatinates have been discussed on the basis of the Galvani potential of ion transfer. Evidence of ion pairing between the platinates and the organic supporting electrolyte cation was found. The thermodynamics of the platinate transfer have also been explored and, in collaboration with Dr Robert Deeth, preliminary density functional theory calculations have been performed to explain the experimental results in terms of a model accounting for the surface charge density of the platinates. This goes further than the classical Born approach of treating the ion as a hard sphere of charge in a dielectric continuum.

The ion transfer across membranes has been studied and the results were applied to single and dual membrane supported liquid/liquid interfaces for separating platinates from base metals. $\left[\mathrm{PtCl}_{6}\right]^{2-}$ transfer across a supported liquid membrane was demonstrated. The scale-up experiments were not successful, but if certain points can be addressed, it may be possible for future studies to build on what has been achieved here.

Additional to the three traditional sections of liquid/liquid work, a method of preparing gold nanoparticles has been found using ketones as the reducing agent at the water/ketone interface. The formation of gold mirrors has been observed and nanoparticles have been isolated and characterised.

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of a university or other institute of higher learning, except where due acknowledgement is made in the text.

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Symbols and Units

| Symbol | Meaning | Value and/or Units |
| :---: | :---: | :---: |
| $a$ | Activity | M |
| $a, a_{1}, a_{2}$ | Reactant radii (Marcus theory) | m |
| $A$ | Interfacial area | $\mathrm{cm}^{2}$ |
| $b$ | Reduced potential (EIS technique) | V |
| $B$ | Marcusian term in reorganisation energy | - |
| C | Concentration | M or $\mathrm{mol} \mathrm{cm}{ }^{-3}$ |
| C | Capacitance | F or $\mu \mathrm{F}$ |
| $C_{\text {b }}$ | Capacitance due to base electrolyte | F or $\mu \mathrm{F}$ |
| $C_{\text {d }}$ | Double layer capacitance | F or $\mu \mathrm{F}$ |
| $C_{\text {int }}$ | Interfacial capacitance | F or $\mu \mathrm{F}$ |
| $C_{\text {s }}$ | Capacitance of faradaic process | F or $\mu \mathrm{F}$ |
| $C_{\text {r }}$ | Capacitance due to adsorbed reactants | F or $\mu \mathrm{F}$ |
| D | Diffusion coefficient | $\mathrm{cm}^{2} \mathrm{~s}^{-1}$ |
| $e$ | Elementary charge (charge on electron) | $1.602 \times 10^{-19} \mathrm{C}$ |
| $e$ | Euler's number | 2.71828182846 |
| $E$ | Potential difference | V |
| $E_{m}$ | Amplitude of sinusoidal potential | V or mV |
| $E_{1 / 2}$ | Half-wave potential | V |
| $F$ | Faraday constant | 96,485 $\mathrm{C} \mathrm{mol}^{-1}$ |
| $I_{m}$ | Max current amplitude (EIS technique) | A or $\mu \mathrm{A}$ |
| $I_{\mathrm{p}}$ | Peak current | A or $\mu \mathrm{A}$ |
| $j$ | Current density | $\mathrm{A} \mathrm{cm}^{-2}$ or $\mu \mathrm{A} \mathrm{cm}{ }^{-2}$ |
| $j_{c}$ | Capacitive current density | $\mathrm{A} \mathrm{cm}^{-2}$ or $\mu \mathrm{Acm}^{-2}$ |
| $j_{f}$ | Faradaic current density | $\mathrm{A} \mathrm{cm}^{-2}$ or $\mu \mathrm{A} \mathrm{cm}{ }^{-2}$ |
| $k$ | Boltzmann constant | $1.38066 \times 10^{-23} \mathrm{~J} \mathrm{~K}^{-1}$ |
| $k^{0}$ | Second order rate constant | $\mathrm{cm} \mathrm{s}^{-1} \mathrm{dm}^{3} \mathrm{~mol}^{-1}$ |
| $k_{s}$ | Observed rate constant | $\mathrm{cm} \mathrm{s}^{-1}$ |
| $K$ | Dissociation constant | No units |
| $n$ | Charge number $\equiv \boldsymbol{z}$ | No units |


| Symbol | Meaning | Value and/or Units |
| :---: | :---: | :---: |
| $n$ | Refractive index $\equiv$ optical dielectric constant | No units |
| $N_{\text {A }}$ | Avagadro's number | $6.022 \times 10^{23} \mathrm{~mol}^{-1}$ |
| $Q$ | Definite integral (Bjerrum theory) | - |
| $r$ | Ionic radius | $\mathrm{m}, \mathrm{nm}$ or $\AA$ |
| $R$ | Internuclear distance (Marcus theory) | M |
| $R_{\text {ct }}$ | Charge transfer resistance | $\Omega$ |
| $R_{\text {s }}$ | Solution resistance | $\Omega$ |
| R | Gas constant | $8.31451 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$ |
| $t$ | Time | Seconds |
| $T$ | Temperature | K |
| W | Warburg impedance | $\Omega$ |
| W1 W2 | Arbitrary terms for cell compartments | - |
| $Y$ | Admittance | Siemens or $\Omega^{-1}$ |
| $z$ | Charge number | No units |
| Z | Impedance | $\Omega$ |
| $Z_{b}$ | Base electrolyte impedance | $\Omega$ |
| $Z_{f}$ | Faradaic impedance | $\Omega$ |
| $Z^{\prime}$ | Real component of complex impedance (Resistive) | $\Omega$ |
| $Z^{\prime \prime}$ | Imaginary component of complex impedance (Capacitive) | $\Omega$ |
| $\alpha$ | Transfer coefficient | No units |
| $\alpha$ and $\beta$ | Arbitrary terms for two solvent phases | - |
| $\gamma$ | Activity of transferring species | No units |
| $\Delta$ | Ellipsometric angle | Degrees ${ }^{\circ}$ |
| $\Delta G_{s}$ | Gibbs energy of solvation | $\mathrm{kJ} \mathrm{mol}^{-1}$ |
| $\Delta G_{\mathrm{t}}$ | Gibbs energy of transfer | $\mathrm{kJ} \mathrm{mol}^{-1}$ |
| $\Delta G^{\ddagger}$ | Free energy barrier | $\mathrm{kJ} \mathrm{mol}^{-1}$ |
| $\Delta \mathrm{e}$ | Magnitude of charge transferred (Marcus theory) | - |
| $\Delta E_{\mathrm{p}}$ | Peak to peak separation | V |


| Symbol | Meaning | Value and/or Units |
| :---: | :---: | :---: |
| $\Delta_{o}^{w} \phi$ | Galvani potential difference | V |
| $\varepsilon$ | Relative permittivity | $\mathrm{C}^{2} \mathrm{~N}^{-1} \mathrm{~m}^{-2}$ |
| $\varepsilon_{0}$ | Permittivity of free space | $8.85419 \times 10^{-12} \mathrm{C}^{2} \mathrm{~N}^{-1} \mathrm{~m}^{-2}$ |
|  | 三 vacuum permittivity |  |
| $\varepsilon_{s}$ | Static dielectric constant (Marcus theory) | $\mathrm{C}^{2} \mathrm{~N}^{-1} \mathrm{~m}^{-2}$ |
|  | $\equiv$ relative permittivity |  |
| $\eta$ | Viscosity | Pa ${ }^{-1}$ or Poise ( P ) where |
|  |  | $1 \mathrm{cP}=10^{-3} \mathrm{~kg} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$ |
| $\theta$ | Phase difference (EIS technique) | Radians |
| $\lambda_{s}$ | Solvent reorganisation energy | $\mathrm{kJ} \mathrm{mol}^{-1}$ |
| $\Lambda$ | Molar conductivity | $\mathrm{cm}^{2} \Omega^{-1} \mathrm{~mol}^{-1}$ |
| $\Lambda^{0}$ | Molar conductivity at infinite dilution | $\mathrm{cm}^{2} \Omega^{-1} \mathrm{~mol}^{-1}$ |
| $\mu^{0}$ | Standard chemical potential | V |
| $\tilde{\mu}$ | Electrochemical potential | V |
| $v$ | Sweep rate | $\mathrm{Vs}^{-1}$ or mV s ${ }^{-1}$ |
| $\sigma$ | Warburg impedance in EIS analysis | $\Omega$ |
| $\Psi$ | Ellipsometric angle | Degrees ${ }^{\circ}$ |
| $\omega$ | Angular frequency | Hz |

## Abbreviations

AAS Atomic absorption spectroscopy

AC / DC Alternating current / direct current
CV
DCE
DFB Difluorobenzene
DFT Density functional theory
DMAMF $\mathrm{N}, \mathrm{N}$-dimethylaminomethyl ferrocene
EIS Electrochemical impedance spectroscopy
ET Electron transfer
FCC Face centred cubic
ITIES Interface between two immiscible electrolyte solutions
MD Molecular dynamics
MIBK Methyl isobutylketone
MM Molecular Mechanics
MSDS Material safety data sheet
MVN \& VN Modified Verwey Niessen \& Verwey Niessen
PEG Polyethylene glycol
PGM Platinum Group Metal(s)
SCE Saturated calomel electrode
SECM Scanning electrochemical microscopy
SLM Supported liquid membrane
TCNQ 7,7',8,8'-tetracyanoquinodimethane
$\mathrm{TEA}^{+} \quad$ Tetraethylammonium cation
TEM Transmission electron microscopy
$\mathrm{THA}^{+}$Tetrahexylammonium cation
$\mathrm{TMA}^{+}$. Tetramethylammonium cation
$\mathrm{TPAs}^{+}$Tetraphenylarsonium cation
TPB- Tetraphenylborate anion
$\mathrm{TPBCl}^{-} \quad$ Tetrakis 4-chlorophenylborate anion
TIC
Transfer by interfacial complexation
TID
Transfer by interfacial dissociation

## 1 Introduction

In industry, large volumes of contaminated wastewater are produced as a result of electroplating common metals, for example nickel and copper or precious metals ${ }^{1}$ such as rhodium, palladium, silver, platinum and gold, during the manufacture of electronic components. Precious metals are used as they have good electronic conductivity and are resistant to corrosion during the life span of the product, which enables them to be used for low impedance, low-noise electronic connections. Examples of such components are the edge connectors in personal computer printed circuit boards, BNC connectors found in laboratory instrumentation and electrical connectors such as plugs and bayonets used in older hi-fi systems. In order to meet environmental legislation and to reduce wastage of valuable materials, it is important to recover and separate metals from waste electrolyte streams. The general principles and benefits of the treatment of waste streams have been outlined in a series of short papers. ${ }^{2-4}$

Traditional electrochemical procedures for recycling plating electrolytes are carried out in aqueous solutions for instance, by electrodeposition at an inert cathode, such as carbon felt ${ }^{5}$ or steel wool. The electrodeposited material or a combination of this and the cathode must then be transported to a refinery for separation. The major shortcoming of this method of recovery is the lack of selectivity as other metals may also be plated out. Other metal reclamation techniques will be mentioned later in this Chapter.

An overview of the literature will be given in this Chapter along with the theory for the major techniques used during the course of this project.

### 1.1 Liquid/Liquid Literature Overview

The liquid/liquid electrochemical interface has often been referred to by the acronym ITIES, derived from the phrase "interface between two immiscible electrolyte solutions." Markin and Volkov ${ }^{6}$ noted that ITIES is not an entirely accurate acronym; their review covered "the electrochemistry of the interface between two partly miscible liquids" where "the mutual solubility of the liquids was rather low and amounts to about a few hundreds of one percent." The acronym ITIES will not be used here.

The topic of liquid/liquid electrochemistry is approaching its centenary; it is highly interdisciplinary with branches in several fields of the physical sciences. Studies have approached the subject from several angles, some from a purely electrochemical viewpoint, others from the background of electroanalysis and still others from a surface science perspective.

Before giving an overview of the topic, mention should be made to some of the major works including books and book chapters covering the topic of liquid/liquid interfaces, ${ }^{7-17}$ comprehensive review articles ${ }^{6,18-20}$ and full issues of journals dedicated to this topic. ${ }^{21,22}$ There are also occasional articles reviewing work to date, for instance Davies and Rideal ${ }^{23}$ covered some of the work up to the early 1950's, Vanysek and Buck ${ }^{24}$ covered work up to the early 1980's, Koryta ${ }^{25}$ reviewed the progress made between 1983 and 1987, and Vanysek ${ }^{26}$ published another review in 1994. In analytical chemistry, the partitioning of a salt or complex from an aqueous solution to an organic phase prior to chemical analysis, uses the same principles and
ideas as those in liquid/liquid electrochemistry. For this reason reviews such as that by Watarai ${ }^{27}$ are also useful.

### 1.1.1 History of the Liquid/Liquid Interface

The original experiment of an electrochemical measurement at the liquid/liquid interface is often ascribed to Nernst and Riesenfeld in 1902; however, the experiments took place and were published by these workers in $1901^{28-30}$ and then expanded in 1902. ${ }^{31,32}$ The electrochemical transport of potassium iodide across "der Grenzfleche zweier Loesungsmittel", which translates as "the interface of two solvents", was studied. A potential was applied between two inert platinum electrodes immersed in the two aqueous phases, see Figure 1.1. The transport of ions across a phenolic organic phase, not directly contacting the electrodes but separating the two aqueous phases, was monitored by measuring the concentration of KI in each aqueous solution with respect to the applied potential.

There were a number of studies made shortly before and after the Second World war; however, research on the topic was sporadic. Selected examples include the work of Karpfen and Randles ${ }^{33}$ on di-isopropyl ketones and nitrobenzene (NB) and, as mentioned earlier, work by Davies and Rideal. ${ }^{23}$ Studies up to 1955 essentially focussed on the distribution potentials observed when an aqueous phase containing organic salts which had an appreciable solubility in a given organic phase was brought into contact with the latter.


Figure 1.1 Nernst and Riesenfeld "U-Rohr" cell (1901).

In the early 1970's there was a renewed interest in the topic as Gavach and coworkers in France used a dropping electrolyte electrode, which was an extension of the ideally polarisable dropping mercury electrode of Heyrovsky. ${ }^{34}$ By the mid 1970's Koryta and co-workers at the J. Heyrovsky Institute ${ }^{35}$ had made a great deal of progress and much of the important early work on the topic was done there. They reported on the electrolysis of an aqueous electrolyte drop electrode ascending into a NB organic phase. ${ }^{36}$

In the early 1980's Senda and co-workers followed the work of Gavach and used a phase-sensitive detection technique for the measurement of kinetic data. Electrocapillary curves for the water/NB interface were measured; ${ }^{37}$ the results indicated that the interface could be treated as ideally polarisable ${ }^{6,38}$ over a certain potential range where ion transfer was negligible. General electrocapillary equations were derived to explain these results. ${ }^{39}$

Phase sensitive ac polarography was used to measure the kinetic parameters of tetramethyl ammonium ( $\mathrm{TMA}^{+}$) and picrate ion transfer across the water/NB interface. ${ }^{40,41}$ A Butler-Volmer relationship was assumed for the potential dependence of the rate equations. Samec et al. measured the transfer of ferricenium cations across the water/NB and water 1,2-dichloroethane (1,2-DCE) interfaces ${ }^{42}$ and later reported the rate of electron transfer between ferrocene (or its derivatives) in the 1,2-DCE phase and hexacyanoferrate(III) in the aqueous phase. ${ }^{43}$ The rate constant was measured using convolution potential sweep voltammetry. The measurements were reported to be complicated by decomposition of the ferrocene species. Also,
from the former work, it would seem likely that some coupled electron and ion transfer process was occurring.

Following Senda's research on picrate ion transfer, ${ }^{41}$ Wandalowski et al. made an electrochemical impedance spectroscopy (EIS) study of the same system. ${ }^{44}$ The kinetic information which can be gained by the application of a small exciting signal to a system in thermodynamic equilibrium makes this technique more reliable than measurements involving large potential sweeps or variations. ${ }^{45}$ Van der Noot and Schiffrin ${ }^{46}$ used a non-linear regression method to fit impedance data for the transfer of base electrolyte and TEA ${ }^{+}$across the water/1,2-DCE interface. The measurements were made from 500 Hz to 0.05 Hz . It was noted that above 500 Hz the only impedance measured was the solution resistance.

Many experimental techniques have been applied to the liquid/liquid interface. Girault and Schiffrin pioneered the measurement of interfacial tension of pendant drops using video capture followed by digital processing of the image, ${ }^{47}$ but more recent interfacial tension measurements have tended to make use of the LangmuirBlodgett technique. ${ }^{48}$ Corn et al. ${ }^{49,50}$ have used second-harmonic generation to follow interfacial adsorption, whilst Girault et al. have specialised in in situ spectroscopy for following charge transfers across the interface. ${ }^{51,52}$ Bard et al. ${ }^{53}$ were the first to apply the technique of scanning electrochemical microscopy (SECM) to the liquid/liquid interface, ${ }^{54,55}$ and recently Shao and Mirkin ${ }^{56}$ have used SECM to follow the facilitated ion transfer of $\mathrm{K}^{+}$by dibenzo-18-crown-6.

### 1.1.2 Electron Transfer

Electron transfer (ET) and ion transfer (IT) are two pathways for the transfer of charge across a liquid / liquid interface. ${ }^{10,57}$ ET reactions at the liquid/liquid interface are of fundamental importance in membrane science and bioelectrochemistry. Marcus reviewed the progress in the field of electron transfer kinetics up to $1964 .{ }^{58}$ ET reactions are unusual because, unlike most chemical reactions, the rupture of bonds is not necessary for the transfer to occur. With the post-WWII availability of radioactive isotopes, isotopic exchange reactions in aqueous solution could be investigated, e.g.

$$
\begin{align*}
& \mathrm{Fe}^{2+}+\mathrm{Fe}^{3+*} \hookrightarrow \mathrm{Fe}^{3+}+\mathrm{Fe}^{2+*}  \tag{1.1}\\
& \mathrm{Ce}^{3+}+\mathrm{Ce}^{4+*} \hookrightarrow \mathrm{Ce}^{4+}+\mathrm{Ce}^{3+*} \tag{1.2}
\end{align*}
$$

where the asterisk indicates an isotope. As the reactants and products of these selfexchange experiments were identical, the influence on the reaction rate of the relative thermodynamic stability of the reactants and products was eliminated. Also, because no bonds are formed or broken during the reaction, these ET reactions are the simplest class of reactions in chemistry. ${ }^{59,60}$

One of the first examples of ET across the liquid/liquid interface was a communication by Guainazzi et al. ${ }^{61}$ A direct current was applied across a water/1,2DCE interface when $\mathrm{Cu}(\mathrm{II})$ was present in the aqueous phase and hexacarbonylvanadate(-I) was present in the organic phase. Under the applied potential, Cu (II) was reduced forming a metal film at the interface. These two solutions were shown to be unreactive when contacted at room temperature; also
when the temperature was raised, the vanadate complex underwent thermal decomposition but this did not result in the reduction of $\mathrm{Cu}(\mathrm{II})$. It was concluded that the copper film formation was due to irreversible ET and the reaction mechanism proposed was:
$\left[\mathrm{V}(\mathrm{CO})_{6}\right]_{(1,2 \mathrm{DCE})}^{-}+2 \mathrm{Cu}^{2+}{ }_{(\mathrm{aq})} \quad \succ \mathrm{V}^{3+}{ }_{(\mathrm{aq})}+6(\mathrm{CO})_{(\mathrm{g})}+2 \mathrm{Cu}_{(\mathrm{s})}$

Reversible ET at liquid/liquid interfaces was first observed by Samec, ${ }^{62}$ who investigated the oxidation of ferrocene to ferricenium in a nitrobenzene phase contacted with aqueous hexacyanoferrate(III) (ferricyanide), which was reduced to hexacyanoferrate(II) (ferrocyanide):

$$
\begin{equation*}
\left[\mathrm{FeCp}_{2}\right]_{(\mathrm{NB})}+\left[\mathrm{Fe}\left(\mathrm{CN}_{6}\right]_{(\mathrm{aq})}^{3-} \hookrightarrow\left[\mathrm{FeCp}_{2}\right]_{(\mathrm{NB})}^{+}+\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}^{4-}\right. \tag{1.4}
\end{equation*}
$$

### 1.1.3 Electroassisted Solvent Extraction

The use of the liquid/liquid interface for the selective extraction and recovery of cations and anions can now be seriously considered as an emerging industrial technology. Figure 1.2 shows the location of an ion of interest, $\mathrm{M}^{+}$, with respect to an applied potential waveform making the aqueous phase positively charged with respect to the organic phase.

It is not usually possible to observe simple ion transfers of hydrated transition metal ions within the polarisation range (potential window) obtained in standard liquid/liquid experiments.


Figure 1.2 Location of a transferring ion $\mathbf{M}^{+}$with respect to a triangular potential/time waveform

The reason is that the Gibbs energy of transfer ( $\Delta G_{\text {trans }}$ ) of the transition metal ion from the aqueous to the organic phase is usually greater than for the transfer of the supporting electrolyte. By using neutral hydrophobic ligands such as terpy $\left(2,2^{\prime} ; 6^{\prime}, 2^{\prime \prime}\right.$-terpyridine $)$ in the organic phase, Cheng et al. ${ }^{63}$ were able to lower the Gibbs energy of transfer of several transition metal ions by complexation with the ligand. These assisted ion transfers were observable within the potential window given by TPAsTPBCl in 1,2-DCE.

### 1.1.4 Theory and Structure of the Liquid/Liquid Interface

In classical electrochemical studies, the conventional definition of the charge at an electrode is based on the theory proposed by Helmholtz, i.e. that of the electrical double layer located at the metal/electrolyte interface. The electrode charge is identified with the charge present on the metallic side of the double layer, which depends on the surface excess or deficiency of electrons at the metal surface. ${ }^{64}$ The double layer was considered to be an inhomogeneous region of electrolyte of defined
thickness adjacent to a charged metal surface, although little was known about the real value of this thickness.

Gibbs proposed a model where the properties of two adjoining phases remained constant up to a mathematical plane which separated them. ${ }^{65}$ All differences between the properties of the real and the model system were ascribed to the surface. This "mathematical surface" had, by definition no volume, which Guggenheim pointed out was unrealistic. ${ }^{66} \mathrm{He}$ described the interface between two liquids as having a surface layer of well defined volume and material content. The use of a model with finite thickness is helpful, especially when considering systems containing charged species due to the long range character of electrostatic forces. ${ }^{67,68}$

Verwey and Niessen ${ }^{69,70}$ (VN) described the electrical double layer of the liquid/liquid interface as two non-interacting diffuse layers located on each side of the interface. The potential distribution of the electrical double layer was defined by the Gouy-Chapman theory.

In the mid-1970's Gavach et al. refined and extended the VN model. They proposed that the liquid/liquid interface was composed of an inner compact layer characterised by a dipolar potential drop between two diffuse layers. ${ }^{71,72}$ Further, they proposed that the inner compact layer contained an organised monolayer of the tetraalkylammonium cations present in the organic phase and an ion free transition layer at the interface. ${ }^{73,74}$ This is equivalent to the compact or inner-Helmholtz layer used in models of the metal/electrolyte interface. Both phases were assumed to be structureless with macroscopic values for the dielectric permittivity. Account was
also taken of the Stern model ${ }^{75}$ of the electrode/solution interface, where the nonelectrostatic particle/electrode (or particle/interface) interaction is approximately independent of the charge on the electrode. ${ }^{76}$ The resulting model became known as the modified Verwey-Niessen (MVN) model.

It should be noted that the MVN model is not a complete description of the liquid/liquid interface but outlines its general structure, on which other more specific features can be constructed. These may take into account ionic interpenetration, effect of ionic size and shape, discreteness of charges and any ion-ion, solvent-ion or solvent-solvent interactions affecting the double layer structure.

Girault and Schiffrin ${ }^{77}$ measured variations in the value of the ion-free layer thickness with solvent polarity and ionic size. Their results suggested that no sharp boundary interfacial layer and no charge free dielectric layers of either solvent were present. Instead, they proposed the presence of a mixed solvent region at these interfaces.

More recently Schmickler, in studies with Henderson ${ }^{78}$ and Pecina, ${ }^{79}$ has provided theoretical treatments of interfacial structure using molecular dynamics (MD) simulations. Their model showed that when the self-interactions of the two solvent molecules were stronger than the cross-interactions, the system separated into two phases, each of which had a high concentration of one component and a lower concentration of the second. If the two components do not mix, the thickness of the interfacial region was calculated to be approximately one solvent molecule in diameter. Michael and Benjamin ${ }^{80-82}$ have done similar calculations using MD.

Another model recently proposed is that of a corrugated structure for the interface due to capillary waves. ${ }^{83}$ The problem of ionic distribution has recently been discussed by Wang et al. ${ }^{84,85}$ who employed a modified Poisson-Boltzmann (MPB) model. It would appear that the structure of the interface is still under debate.

### 1.1.5 Charge Transfer

In order to describe the transfer of charge across the liquid/liquid interface, the process occurring at a metal/solution interface must first be considered. The origin of electrode potentials can be found in many fundamental physical chemistry texts. ${ }^{86-89}$

At a metal electrode, the interfacial potential difference originates from the difference in electronic energy between a redox couple in solution and the metal. The metal can act as a source or sink of electrons for the solution species until the ionic levels of the redox couple and the Fermi level of the metal electrode are at equilibrium. The result is that the metal loses (or gains) electron density; when equilibrium is reached, there will be a difference in charge and therefore a difference in potential between the metal and the solution phases.

At a liquid/liquid interface, the origin of the potential difference is due to the partitioning of the ions of a salt between the two phases. Girault and Schiffrin made a full treatment of the interfacial potential. ${ }^{10}$ The fundamental properties which we must consider are the solvation energies of the salt under examination, the distribution (or partition) coefficients of the salt and the electrical potentials which arise from the ionic partitioning.

When a solute is added to one of the phases of a liquid/liquid system, it will have a finite solubility in the opposite phase and will, to some degree, partition into it. For example, when two solutions are contacted, e.g. 1,2-DCE with an aqueous solution of TMACl, the exchange of TMACl will eventually reach equilibrium. At this point, the rate of transfer of TMACl from the aqueous to the organic phase is equal to the rate of transfer of TMACl in the opposite direction. The electrochemical potentials of ions in the phases must also be equal:
$\tilde{\mu}_{1}=\tilde{\mu}_{2}$

This can be rewritten in terms of the standard chemical potentials $\mu_{1}^{0}$ and $\mu_{2}^{0}$, and the ionic activities $a_{1}$ and $a_{2}$ of the ion in the two phases 1 and 2:
$\mu_{1}^{0}+R T \ln a_{1}+z F \phi_{1}=\mu_{2}^{0}+R T \ln a_{2}+z F \phi_{2}$

For a neutral species $z=0$, and from (1.6):
$\mu_{1}^{0}-\mu_{2}^{0}=R T \ln a_{2}-R T \ln a_{1}$
and

$$
\begin{equation*}
\frac{\mu_{1}^{0}-\mu_{2}^{0}}{R T}=\ln \left(\frac{a_{2}}{a_{1}}\right) \tag{1.8}
\end{equation*}
$$

$$
\begin{equation*}
\frac{a_{2}}{a_{1}}=\exp \left(\frac{\mu_{1}^{0}-\mu_{2}^{0}}{R T}\right) \tag{1.9}
\end{equation*}
$$

For an ionic species, $i$, of charge $z_{i}$, the Galvani potential difference is given by the two phase Nernst equations: ${ }^{10}$
$\Delta_{o}^{w} \phi=\Delta_{o}^{w} \phi_{i}^{0}+\frac{R T}{z_{i} F} \ln \left(\frac{a_{i}^{(0)}}{a_{i}^{(w)}}\right)$

The difference between the standard chemical potentials is known as the standard Gibbs energy of transfer. This thermodynamic quantity is denoted by the symbol $\Delta G_{i}^{0}$, where:
$\Delta_{o}^{w} \phi=-\left(\frac{1}{z_{i} F}\right) \Delta_{o}^{w} G_{i, i}^{0,0 \rightarrow w}$

In order to compare experimental and thermodynamic data, a common thermodynamic scale is required. The scale which has evolved for liquid/liquid electrochemistry is known as the Galvani scale. ${ }^{90}$ : This relates the interfacial potential to the Gibbs energy of transfer between phases. $\Delta_{\beta}^{\alpha} \phi$ is the electrical potential difference between points within the bulk phases $\alpha$ and $\beta$. It is measurable only if the phases are of identical composition unless an extrathermodynamic assumption is made. ${ }^{91}$ The zero of the Galvani scale is equivalent to the zero of the standard hydrogen electrode.

The Galvani scale has been established from partition studies for which a "reference electrolyte" ${ }^{92}$ was used. This idea was based on the thought experiment of Grunwald ${ }^{93}$ who suggested that individual ionic partition coefficients could be
obtained from partition data for tetraphenyl methane (TPM), tetraphenyl phosphonium (TPP ${ }^{+}$) and TPB ${ }^{-}$(Figure 1.3). The Gibbs energy of solvation of the cation and the anion were considered the same due to the similarity of size and molecular structure. The non-electrostatic component of solvation of large ions with low surface charge density would closely resemble that of an uncharged molecule of equal size and structure, as shown in Figure 1.4 below.

This is similar to the proposal of Parsons et al. ${ }^{94}$ who calculated the difference of real solvation energies of alternant hydrocarbon ions (hydrocarbons which can be made both cationic and anionic). The difference in chemical solvation of the cation and anion form was found to be essentially zero.

Arnett and McKelvey ${ }^{95}$ and Parker and Alexander ${ }^{96,97}$ extended this theory to the solvation of TPAsTPB in non-aqueous solvents. Up to that time, it had been customary to calculate single ionic enthalpies of transfer; series of cations were compared with each other through their salts of a common anion, and similar but separate scales were constructed for anions. By utilising Grunwald's assumption that TPAs $^{+}$and TPB ${ }^{-}$had equal enthalpies of transfer, it was possible to place anions and cations onto a common scale.

For the water/1,2-DCE interface the ionic standard Galvani transfer potentials for TPAs $^{+}$and TPB ${ }^{-}$are +0.363 V and -0.363 V respectively. ${ }^{10}$ This principle was later used to measure the extraction constants and partition data for a large number of ions across the water $/ \mathrm{NB}^{98}$ and water/1,2-DCE ${ }^{99}$ interfaces.




Figure 1.3 Species employed in the estimation of individual ion transfer properties.


Figure 1.4 A stick and dot representation of tetraphenylmethane.

Abraham and de Namor ${ }^{100}$ obtained the free energy of solution of salts by measuring the solubility of an electrolyte in an organic phase, correcting for the association constant of the salt $\mathrm{M}^{+} \mathrm{X}^{-}$and for the activity coefficients using the extended DebyeHuckel theory. ${ }^{86}$ Once equivalent data was obtained by dissolving the same salt in water, the free energy of transfer of the salt from the aqueous to the organic phase was calculated. From this information, the Gibbs energy of transfer of individual ions could then be obtained by employing the TPAsTPB assumption described above. Hence, by measuring the potential window for a given solvent using TPAsTPB as the supporting electrolyte in the organic phase, a zero could be established for the Galvani scale in that particular solvent and Gibbs energies of transfer for other ions could be calculated relative to that value. ${ }^{101}$

### 1.1.6 Simple Ion Transfers

Koryta et al. ${ }^{102}$ outlined the principles of faradaic ion transfer reactions. Simple ion transfer occurs when the applied potential across the interface is sufficient to overcome the Gibbs energy of transfer $\Delta G_{\text {trans }}$ of the ion under observation. Samec et al. ${ }^{103}$ measured the transfer of $\mathrm{Cs}^{+}$across the water/NB interface, whilst Kakutani et al. ${ }^{104}$ studied the transfer of the $\mathrm{TMA}^{+}$ion across the water/NB interface using chronoamperometry. The $\mathrm{TMA}^{+}$and picrate ion transfer studies of Senda et al. were mentioned earlier in this Chapter. ${ }^{40,41}$

Kontturi et al. ${ }^{105}$ measured the kinetics and mechanism of potassium ion transfer across the water/1,2-DCE interface. A pre-equilibrium reaction, where an ion pair was formed between $\mathrm{K}^{+}$and the organic supporting electrolyte cation (TPB) in the interfacial region was proposed.

Larger ions have also been investigated, for example, Wang and Liu examined the transfer of terramycin (oxytetracycline, a multipurpose antibiotic) across the water/NB interface ${ }^{106}$ whilst Osakai et al. observed the transfer of heteropoly- and isopoly anions across the water/NB and water/1,2-DCE interfaces. ${ }^{107,108}$ Recent work by Girault et al. has focussed on the transfer of ionisable drugs such as quinine and trimetazadine. ${ }^{109}$

### 1.1.7 Facilitated Ion Transfer

Several models have been proposed for facilitated cation transfer across a liquidliquid interface. One example is the reversible transfer of potassium ions across the water/NB interface facilitated by the macrocyclic polypeptide antibiotic valinomycin. Koryta et al. ${ }^{110,111}$ had proposed that $\mathrm{K}^{+}$was transferred electrochemically, followed by complexation with valinomycin in the organic phase. For the same system, Yoshida and Freiser ${ }^{112}$ suggested that complexation took place in the aqueous phase followed by an electrochemical transfer of the complex to the organic phase.

Girault ${ }^{11,113,114}$ suggested a more general mechanism of "transfer by interfacial complexation - transfer by interfacial dissociation" (TIC - TID). For the forward TIC step, as the aqueous phase is made more positive with respect to the organic phase, the cation is transferred through the aqueous or source phase towards the interface where it complexes with a lipophilic ligand or extractant. The cation-ligand complex then diffuses away from the interface into the bulk of the organic phase. For the reverse TID step, as the aqueous phase is made less positive with respect to the organic phase, the cation-ligand complex is transferred through the organic phase back towards the interface. The cation is soluble in the aqueous phase but the ligand
is not. Dissociation of the cation-ligand complex allows the cation to transfer back to the aqueous phase whilst the hydrophobic ligand remains in the organic phase.

If a stacked cell of aqueous/organic/aqueous phase were to be used, where the organic phase contained a cation selective ligand, a cation of interest could then be transferred under potential control from the first aqueous phase, through a hydrophobic phase and on into a second aqueous receiver phase. This is the underlying principle of electroassisted extractions using supported liquid membranes which will be further discussed in section 1.1.10.

Koryta studied the transfer of potassium ions from water to NB facilitated by the macrocyclic crown ether dibenzo-18-crown-6. ${ }^{115}$ In subsequent work, ${ }^{116}$ EIS was used to obtain kinetic data for the same crown ether in NB, this time facilitating the transfer of $\mathrm{Na}^{+}$and possible transfer mechanisms were discussed. Katano and Senda ${ }^{117}$ used a macrocyclic thioether, a sulfur analog of a crown ether, to facilitate the transfer of $\mathrm{Pb}(\mathrm{II})$ from water to NB . The importance of these results is to show that the metal-ion coordination chemistry can be used to further control transfer.

Marecek and Samec used a macrocyclic polyether diamide to facilitate the transfer of group 2 divalent cations. ${ }^{118}$ In a series of publications, Makrlik and Hung ${ }^{119-121}$ showed that the transfer potential of some cations were affected by the organic phase supporting electrolyte anion, e.g. the transfer of $\mathrm{Cs}^{+}$occurred at a potential 40 mV more negative when using TBATPB than when using tetrabutylammonium dicarbollylcobaltate (TBADCC). This facilitation of the transfer was attributed to ion-pairing between $\mathrm{Cs}^{+}$and TPB .

Wang and Liu ${ }^{122}$ observed a reversible diffusion controlled transfer of $\mathrm{Cd}(\mathrm{II})$ facilitated by $2,2^{\prime}$-bipyridine. Sun and Wang ${ }^{123}$ used polyoxyethylene ionophores to facilitate the transfer of barium and strontium across the water/NB and water/1,2DCE interfaces and later Sun and Vanysek ${ }^{124}$ used polyethylene glycols (PEGs) as neutral carriers to facilitate the transfer of $\mathrm{Pb}(\mathrm{II})$ across the water $/ \mathrm{NB}$ interface. Cheng and Schiffrin ${ }^{63}$ employed nitrogen-containing ligands to facilitate the transfer of a number of transition metal ions across the water/2-heptanone and water/2octanone interfaces. More recently Wilke and Wang ${ }^{125}$ used a cadmium selective ionophore to facilitate the transfer of some heavy metals across the water/NB interface.

### 1.1.8 The Solvent / New Solvents

Liquid/liquid studies have traditionally been performed in NB and 1,2-DCE. Unfortunately, NB is a carcinogen and 1,2-DCE is also highly toxic. If liquid/liquid techniques are to be successfully transferred to an industrial scale, less toxic solvents will be required. Desirable properties besides low toxicity are: low miscibility with water and dielectric permittivity ( $\varepsilon$ ) greater or at least equal to that of $1,2-\operatorname{DCE}\left(\varepsilon_{1,2}\right.$ $D_{C E}=10.42$ Debye $)$.

Ketones are one alternative group of solvents; Karpfen and Randles ${ }^{33}$ examined the influence on the distribution of electrolytes across the water/di-isopropyl ketone interface on the change in interfacial potential. Koczorowski et al. examined the water/isobutylmethylketone (IMK, also known as 4-methyl-2-pentanone, hexone or methyl isobutylketone, MIBK) interface. ${ }^{126}$

The latter work showed that there was no practical potential window in which the current could be controlled by charging of the interface alone. The Gibbs energy of transfer of the supporting electrolyte was lowered so much that the ends of the potential window were insufficiently separated and an ion transfer free range could not be obtained with the electrolytes used ( LiCl and TBATPB). This was attributed to the increased solubility of water in MIBK, which decreased the differences between ionic distribution coefficients, thereby narrowing the potential polarisation range.

Cheng ${ }^{127,128}$ recently examined the water/2-octanone interface. 2-octanone has low toxicity but the potential window is unsatisfactory for some applications, such as drug transfer studies, where a wide potential window is necessary.

Useful data for the solubility of ions in MIBK were provided by Courtot-Coupez et al. ${ }^{129}$ who studied the solvation of ions in anhydrous and water-saturated MIBK. They also investigated the electrochemical behaviour of the solvent itself. It was concluded that MIBK was electrochemically stable and that a potential range of 5.3 V could be obtained with Pt electrodes and tetrabutylammonium perchlorate $\left(\mathrm{Bu}_{4} \mathrm{NClO}_{4}\right)$ as the supporting electrolyte. Their work concluded that the strength of ionic solvation in MIBK was related to the amount of water in the solvent. Results obtained in the present work demonstrate that varying the supporting electrolyte can widen the potential window for MIBK.

The interest in the use of congeners of NB is that they offer not only a safer alternative, but also the opportunity for comparison of rates of ET with solvents
based around a common organic structure. In a short communication by Armstrong ${ }^{130}$ and in another work by Horvai, ${ }^{131}$ the solvent properties of $o$ nitrophenyl octyl ether (o-NPOE) were investigated. o-NPOE is a viscous liquid used as a plasticising agent in PVC membranes for ion selective electrodes, e.g. for the determination of $\mathrm{Ca}^{2+}$. Valent and Koryta ${ }^{132}$ were the first to employ $o-N P O E$ as a liquid/liquid solvent and tested Parker's TPAsTPB assumption. o-NPOE became widely used for liquid/liquid studies some ten years later on. ${ }^{133,134}$ Bartsch et al. ${ }^{135}$ made a major study of 2-nitrophenyl alkyl ethers. Structural variation of the alkyl group on the ether was found to affect the efficiency and selectivity of alkali metal ion transport across polypropylene-supported liquid membranes by a lipophilic crown ether carboxylic acid. Although this was not an electrochemical study, many useful values of solvent viscosities and dielectric permittivity s were provided.

Samec noted that $o-$ NPOE is less miscible with water than $1,2-\mathrm{DCE}$ and that it has a higher dielectric permittivity than 1,2-DCE of 24.2, ${ }^{136}$ although Bartsch puts this value at 31.78. ${ }^{135}$ There are, however, several disadvantages to the use of $o-\mathrm{NPOE}$, not least of which is the cost of approximately $£ 4 \mathrm{~cm}^{-3}$. Also, o-NPOE has a density of $1.041 \mathrm{~g} \mathrm{~cm}^{-3}$, very close to that of water, which makes it difficult to form a welldefined interface in a standard four-electrode cell. Most importantly, o-NPOE has a high viscosity ( $\eta_{2 \text {-NPOE }}$ ) of between 12.35 and $13.8 \mathrm{cP}^{133,135}$ in comparison with $\eta_{\mathrm{NB}}$ $=1.795$ and $\eta_{1,2-\mathrm{DCE}}=0.779 \mathrm{cP}$. This high viscosity is likely to impede the diffusion of species in the organic phase towards the interface, decreasing the rate of any interfacial process under investigation. To avoid this problem and for comparison purposes, the present work employed o-nitrophenyl pentyl ether (o-NPPE) as its viscosity is considerably lower than that of $o-\mathrm{NPOE}\left(\eta_{2-\mathrm{NPPE}}=7.58 \mathrm{cP}\right)$.

Alemu et al. ${ }^{137}$ investigated the water/o-nitrotoluene interface using EIS to measure the interfacial capacitance for several supporting electrolytes. A negative shift in the minimum of interfacial capacitance, or potential of zero charge (PZC) was observed with increasing supporting electrolyte concentration. This effect is characteristic of the presence of specific ionic adsorption. ${ }^{138,139}$ Esin-Markov tests on the data showed that the value of the capacitance for o-nitrotoluene was similar to that obtained for NB and independent of supporting electrolyte; therefore ionic adsorption was not present. The material safety data sheet (MSDS) for o-nitrotoluene show that it is a suspected carcinogen; however, the meta-isomer of nitrotoluene is less toxic, and for this reason $m$-nitrotoluene was studied in the present work. The para- isomer of nitrotoluene is a solid at room temperature and was not studied.

Sun and Wang ${ }^{140}$ studied a number of solvents including $o$-dichlorobenzene, benzyl cyanide, phenyl isothiocyanate, propiophenone, methyl cyclohexone, cyclohexane and methyl amyl ketone (methyl pentyl ketone). Although most of the potential windows obtained gave an ion transfer free polarisable region of the order of $100-$ 200 mV , which for most liquid/liquid purposes is unusable, some results for mixtures of solvents were reported. The magnitude of the potential windows obtained was dependent on the ratio of solvents used, e.g. for a mixture of chlorobenzene (CB) and benzonitrile ( BN ), the size of the potential window for the ratio $\mathrm{CB}: \mathrm{BN}$ increased in the order of 6:4>4:6>8:2>2:8. Hundhammer et al. ${ }^{101}$ observed ion transfer across the water/o-dichlorobenzene interface. By a judicious choice of electrolyte anions and cations, they made an elegant study of the transfer processes occurring at each end of the potential window. Tan et al. ${ }^{141}$ also used o-dichlorobenzene in their investigation of the Williamson ether synthesis. The synthesis uses strongly alkaline
conditions in the aqueous phase ( 12.5 M NaOH ). The potential window of approximately 800 mV was available due to the salting out of the organic supporting electrolytes by the high concentration of NaOH in the aqueous phase.

Cheng ${ }^{142}$ suggested that liquid/liquid studies might be made using media of low dielectric permittivity in order to extend the potential window over which ET could be observed. The work of Abbott and Schiffrin ${ }^{143-145}$ was cited as an example of low dielectric permittivity solvents. The systems studied were mixtures of biphenyl, naphthalene and phenanthrene with anisole. In order to study a low dielectric permittivity solvent, the present work has made use of the ortho- and meta- isomers of difluorobenzene ( $o-$ DFB and $m$-DFB) and a binary mixture of $o-D F B / 1,2-\mathrm{DCE}$ as the organic solvents. The dielectric permittivity of $m$-DFB is slightly above 5 , which is relatively low in terms of the organic solvents commonly used for liquid/liquid electrochemistry.

It can be seen from the literature that a large number of solvents have been tested for their suitability for liquid/liquid experiments. The current alternatives to $1,2-\mathrm{DCE}$ and NB are o-NPOE which is relatively expensive, o-dichlorobenzene which although not carcinogenic, is still very toxic, and the ketones of Cheng et al. which provide a relatively small potential window. It would be of general use to workers in the field if an alternative solvent could be located.

### 1.1.9 Metal Ion Recovery

There are many techniques for reclaiming metals from solution. Examples include the use of ion exchange resins, ${ }^{146}$ solvent extraction, chelate extraction, ${ }^{147}$ ion association, reverse osmosis ${ }^{148}$ and crossflow microfiltration, ${ }^{149}$ but usually for the recovery of certain metals in niche applications. At the beginning of the 1970's, solvent extraction techniques started to be used in precious metal separation, concentration and purification. Al-Bazi and Chow ${ }^{150}$ made a thorough review of solvent extraction and ion-exchange of platinum group metals for the period 19501983. Schiffrin et al. ${ }^{151}$ proposed an electroassisted solvent extraction (ESE) strategy for heavy metal separation. Due to the availability of a large number of ligands, high selectivity and efficiency might be achieved in various solvent extraction systems. Two large categories of extractants for precious metals separation have been developed: amine derivatives and sulphur containing compounds. The properties of these extractants depend largely on their abilities either to form chelate complexes with metals or to extract anionic complexes by ion-association reactions. Kettrup et al. ${ }^{152}$ discussed the extraction and separation of $\mathrm{Pt}(\mathrm{IV}), \mathrm{Pd}(\mathrm{II})$ and $\mathrm{Ag}(\mathrm{I})$ into dichloromethane and toluene by sulfonated and unsulfonated formazan chelating agents. They noted that "in the presence of surfactants and chelating agents, metal ions could be favourably coordinated at the interface of the two phases and not in the aqueous phase".

Frieser et al. ${ }^{153}$ have been prominent in the recovery and separation of PGMs; platinum and palladium were both found to be extracted into heptane by the ligand bis(2,4,4-trimethypentyl)-phosphinodithioic acid. The same group used centrifugal
partition chromatography to extract PGMs into heptane employing the extractant trioctylphosphine oxide (TOPO). ${ }^{154}$

In a chromatographic study, Rogers et al. ${ }^{155}$ recognised some of the problems presented by the use of toxic or flammable organic solvents for liquid/liquid metal ion extraction. Similarly to Wang ${ }^{123}$ and Vanysek, ${ }^{124}$ they also investigated PEGs, but by partitioning the PEG using the salting out effect, an aqueous biphasic system (ABS) was formed where the major component in each of the two phases was water and no separate organic solvent was required.

The recovery of PGMs is also of importance in industries other than electroplating. Cooley reviewed methods for the recovery of Ag from wash water generated by the photographic industry ${ }^{156}$ and Yoshida et al. ${ }^{157}$ described the electroreduction of PGMs onto a flow through electrode for use in the reprocessing of nuclear fuels; reference was made to the electroextraction of $\mathrm{Cs}^{+}$and $\mathrm{Sr}^{2+}$ by electrolytic ion transfer into 1,2-DCE. ${ }^{158}$ Zhou and Chin ${ }^{159}$ described a continuous electrolytic process for the recovery of metals from ternary mixtures of $\mathrm{Ag}, \mathrm{Cu}$ and Cd cyanides. Suzuki et al. ${ }^{160}$ tackled a similar problem involving $\mathrm{Ag}, \mathrm{Cu}$ and Zn . In both studies, the initial metal concentration was of the order of several hundred parts per million (ppm), with the required final concentration set at 1 ppm or lower. For dilute solutions, enhanced mass transport is an important consideration and various cell and electrode designs were discussed to achieve an efficient separation.

A variety of neutral sulphur compounds have been used in solvent extraction systems for precious metal separation. Thiourea derivatives are one of the best groups of
ligands for the complexation of precious metals, for instance, diphenylthiourea ${ }^{161}$ and N -substituted benzoyl thiourea for the separation of PGMs. ${ }^{162}$ Sulphur-containing carboxylic acids, ${ }^{163}$ diethylthietane (DETE) ${ }^{164}$ and 2-mercaptobenzothiazole ${ }^{165}$ have also been employed in the past for precious metal extraction and analytical determinations.

Experimental conditions such as solution pH , anion concentrations and the supporting electrolytes employed are of importance in extraction processes. Freiser and co-workers ${ }^{166}$ carried out a systematic study of palladium extraction using different ligands in the presence of quaternary ammonium salts, which can accelerate extraction rate through the formation of highly extractable complexes between anions and tetraalkylammonium cations. Yamamoto and Katoh ${ }^{167}$ made a similar study, investigating the distribution behaviour of hexachloroplatinate with quaternary ammonium cations across the water/chloroform and water/carbon tetrachloride interfaces. This will be discussed further in Chapter 5.

In chloride media, precious metals are usually present as anions, some of which are inert to ligand replacement. Ahmed and Koch ${ }^{168}$ reported the separation of metals on the basis of differing rates of formation of extractable species during ligand replacement reactions.

Viets et al. ${ }^{169,170}$ used MIBK in their multielement analytical extraction method with the commercial extractants Alamine 336 (a tertiary monoamine extractant) and Aliquat 336 (a quaternary monoammonium chloride salt). In a similar study, Kalpana and Koshy used dithizone to extract platinum into MIBK. ${ }^{171}$ Shillington and Tait ${ }^{172}$
conducted chelate extraction of individual PGMs using the tertiary diamine salts $N, N$-di-n-octyl-2-(aminomethyl)pyridine (pyridioc) and $N, N, N, N$ '-tetra-noctylethylenediamine (tetocen) to extract selectively $\mathrm{Pd}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{IV})$ from a base metal solution of $\mathrm{Cu}(\mathrm{II}), \mathrm{Ni}$ (II), Co (II) and Fe (III) in 1 M LiCl solutions, a comparison was made with Alamine 336 and Aliquat 336. It was found that at pH 1.0 , pyridioc gave selective extraction of $\mathrm{Pd}(\mathrm{II})$ and tetocen selectively extracted $\mathrm{Pt}(\mathrm{IV})$. At pH 4.7 both extractants were selective to $\mathrm{Pd}(\mathrm{II})$ and displayed better selectivity than Alamine 336 and Aliquat 336.

Côté and Demopoulos ${ }^{173}$ extracted $\mathrm{Pd}(\mathrm{II})$ from aqueous chloride media using chloroform solutions of 7 -substituted-8-hydroxyquinoline (8-HQ) derivatives. A discussion was presented on the variation of chelating power of $8-\mathrm{HQ}$ derivatives due to a change in the inductive effect of the nitrogen and hydroxyl groups. The steric effects on the introduction of alkyl groups at the 2-, 5- and 7-positions on the oxine ring system were also discussed. Sawada and Osakai ${ }^{174}$ discussed the mechanism of transfer of some divalent metal ions across the water/NB interface facilitated by quinolin-8-ol ( HQ ). The proposed mechanism involved the transfer of HQ to the aqueous phase by partitioning, dissociation of the HQ in the aqueous phase and formation of a $1: 1$ complex between $\mathrm{M}^{2+}$ and $\mathrm{Q}^{-}$i.e. $\mathrm{MQ}^{+}$. The facilitated transfer of $\mathrm{MQ}^{+}$was observed electrochemically.

Ulakhovich et al. ${ }^{175}$ reviewed the methods of concentrating PGMs prior to voltammetric analysis, whilst Benguerel et al. ${ }^{176}$ reviewed the speciation and separation of Rh (III) from chloride solutions. Rhodium chloride has a complicated
solution chemistry, the result of which is that rhodium cannot be easily recovered by traditional ligand replacement solvent extraction methods.

### 1.1.10 The Supported Liquid Membrane

Fane et al. ${ }^{177}$ outlined the requirements for metal recovery from wastewater using membranes with particular reference to electroplating wastes. There are several membrane based methods in use, including nanofiltration (NF), ultrafiltration (UF) and supported liquid membranes (SLMs). SLMs were suggested as early as 1986 by Babcock et al., ${ }^{178}$ utilising the same chemistry as solvent extraction methods. SLMs consist of a microporous substrate which is used to physically immobilise a thin organic liquid layer within a membrane wall, thereby stabilising the liquid-liquid interfaces. Such an SLM has a dual functionality, as it would give metal separation and concentration in a single device.

A feature of the SLM is that it requires only small amounts of the organic ligand and therefore more complex or expensive extractants can be utilised. The main disadvantage is that the membranes have a limited lifetime and are susceptible to fouling. SLMs can also be susceptible to the alkaline or acidic additives used in plating processes, including brighteners, levellers and suppressants. Possible fouling agents/contaminants include: sodium lauryl sulphate, aromatics (in nickel baths), citric acid, tartaric acid, oxalic acid and saccharides (in chromium baths).

### 1.2 Electrochemical Techniques

The advent of the four electrode potentiostat has allowed the application of standard electrochemical techniques to the liquid/liquid interface. The two main techniques used in the present work were cyclic voltammetry and electrochemical impedance spectroscopy (EIS).

### 1.2.1 Cyclic Voltammetry

Cyclic voltammetry is generally used for preliminary electrochemical studies. In the three electrode configuration, a triangular potential profile is applied between the working and counter electrodes with reference to a known redox potential provided by a high impedance reference electrode, positioned close to the surface of the working electrode. Further experimental detail will be given in Chapter 2. The current response is recorded against the applied potential. The cyclic voltammogram (referred to as the CV ) can be used to determine the potentials at which redox or adsorption processes occur at electrode surfaces; it can yield information about the reversibility of electrode processes. The diagnostic test for a reversible transfer process is the separation of forward and reverse peak currents $\left(E_{p}{ }^{a}\right.$ and $E_{p}{ }^{c}$ respectively), $\Delta E_{\mathrm{p}}$, given by:
$\Delta E_{p}=E_{p}{ }^{a}-E_{p}^{c}=59 / n \mathrm{mV}\left(\right.$ at $\left.25^{\circ}\right)$
$n$ is the number of electrons exchanged or transferred per mole of reacting species. Diffusion coefficients of redox species can be obtained from the dependence of peak current on sweep rate using the Randles-Sevcik equation: ${ }^{179}$
$i_{p}=2.69 \times 10^{5} n^{3 / 2} A D^{1 / 2} v^{1 / 2} C$
where $i_{p}$ is the peak current (A), $A$ is the interfacial area $\left(\mathrm{cm}^{2}\right), D$ is the diffusion coefficient $\left(\mathrm{cm}^{2} \mathrm{~s}^{-1}\right), v$ is the sweep rate $\left(\mathrm{V} \mathrm{s}^{-1}\right)$ and $C$ is the concentration of the transferring species ( $\mathrm{mol} \mathrm{cm}{ }^{-3}$ ). Under quasi-reversible or fully irreversible conditions, cyclic voltammetry can also be used to obtain kinetic information for a given redox process.

### 1.2.2 Electrochemical Impedance Spectroscopy

The perturbation technique of electrochemical impedance spectroscopy (EIS) or AC impedance spectroscopy has been widely used to examine the solid/liquid (electrode/electrolyte) interface. Descriptions of the theory of the technique can be found in References 180-184. EIS involves the application of an oscillating sinusoidal potential, $E(t)$ :

$$
\begin{equation*}
E(t)=E_{m} \sin (\omega t) \tag{1.14}
\end{equation*}
$$

where $\omega$ is the angular frequency in $\mathrm{Hz}\left(\mathrm{s}^{-1}\right)$ and $E_{m}$ is the maximum amplitude, and measuring the current $i(t)$. This is given in general by:

$$
\begin{equation*}
i(t)=i_{m} \sin (\omega t+\theta) \tag{1.15}
\end{equation*}
$$

where $i_{m}$ is the maximum current amplitude and $\theta$ represents the phase difference between the applied potential and the current measured.

For a pure capacitance the current is given by:
$i=\frac{\mathrm{d} q}{\mathrm{~d} t}=C_{d} \frac{\mathrm{~d} E}{\mathrm{~d} t}=C_{d}\left\{\omega E_{m} \cos (\omega t)\right\}$
which can be rewritten as:
$i=C_{d}\left\{\omega E_{m} \sin (\omega t+\pi / 2)\right\}$
where the phase difference, $\theta=\pi / 2$. For a pure resistor $\theta=0$. The response of an electrical circuit is usually given in terms of the impedance $Z$ :

$$
\begin{equation*}
Z(f)=\frac{E(t)}{i(t)} \tag{1.18}
\end{equation*}
$$

For a simple capacitor, $Z=1 /\left(\omega C_{d}\right)$. For an electrochemical system the phase difference can take any value and is frequency dependent. The impedance $Z(\omega)$ is described by a Nyquist plot of $-Z^{\prime \prime}$ versus $Z^{\prime}$ where $Z(\omega)$ is equal to a vector from the origin to a given point with coordinates $\left(Z^{\prime},-Z^{\prime \prime}\right)$ :

$$
\begin{equation*}
Z(f)=Z^{\prime} \sin (\omega t)-Z^{\prime \prime} \cos (\omega t) \tag{1.19}
\end{equation*}
$$

$Z$ ' and $-Z$ ' are known as the 'in phase and out of phase' or 'real and imaginary' components respectively. The Nyquist plot is characteristic for a particular electrical circuit.

EIS has been widely used for the study of ion transfer reactions across the liquid/liquid interface. Girault et al. ${ }^{185}$ extended the technique to ion transfer across micro-interfaces and Cheng et al. ${ }^{186,187}$ employed it for the determination of the rate constants for some ET reactions. For the purpose of the EIS analysis of charge transfer, the interface may be represented as an equivalent electrical circuit. ${ }^{188}$ The model used is a modified Randles circuit (Figure 1.5).


Figure 1.5 Equivalent circuit used for EIS

It comprises a solution resistance, $R_{s}$, in series with three parallel components:
(i) The interfacial capacitance $C_{i n t}$ with contributions from the base electrolyte, $C_{b}$, and from adsorbed reactants, $C_{r}$. There is a contribution from the capacitive part of the Faradaic impedance of the charge transfer process; included in (iii).
(ii) The Faradaic impedance due to the transfer of the base electrolyte, $Z_{b}$ and a related Warburg component, W, related to the diffusion of the base electrolyte.
(iii) The Faradaic impedance due to the charge transfer process of interest, $Z_{f}$. This circuit component consists of two elements in parallel: a charge transfer resistance, $R_{c t}$ and a capacitance associated with the Faradaic process, $c_{s}$. These are in series with a Warburg impedance due to semi-infinite linear diffusion.

For the electron transfer measurements, the EIS data were treated following the methods used by Seno et al. ${ }^{189}$ and Cheng and Schiffrin. ${ }^{186,187}$ The measured impedance comprises components from the impedance of the base electrolyte and of ion transfers, as well as the impedance due to the electron transfer of interest. The impedances in Figure 1.5 are in parallel. To obtain the Faradaic admittance of the ET process, the ion transfer component must be subtracted. To achieve this, the impedances must first be converted to admittances (the reciprocal of impedance) for subtraction. ${ }^{190}$
$Y_{f}^{\prime}=Y_{t}^{\prime}-Y_{b}^{\prime}$
$Y_{f}^{n}=Y_{t}^{n}-Y_{b}^{n}$
where $Y$ represents the admittance and the subscripts $f, t$ and $b$ are used to denote the Faradaic, total and base - electrolyte admittances. The Faradaic impedance is composed of a resistive component, $r_{s}$, which is related to the real part of the impedance $Z^{\prime}$ and a capacitive, $1 / \omega c_{s}$, related to the imaginary part of the impedance, $-Z^{\prime \prime}$. These are obtained from: $:^{187,189}$

$$
\begin{align*}
& r_{s}=\frac{Y_{f}^{\prime}}{\left(Y_{f}^{\prime}\right)^{2}+\left(Y_{f}^{\prime \prime}\right)^{2}}  \tag{1.22}\\
& \frac{1}{\omega c_{s}}=\frac{Y_{f}^{n}}{\left(Y_{f}^{\prime}\right)^{2}+\left(Y_{f}^{n}\right)^{2}} \tag{1.23}
\end{align*}
$$

where $\omega$ is the angular frequency and $c_{s}$ is the capacitance due to the Faradaic process. These quantities are related to the charge transfer reaction through:
$r_{s}=R_{c t}+\frac{\sigma}{\omega^{0.5}}$
$\frac{1}{\omega c_{s}}=\frac{\sigma}{\omega^{0.5}} \quad$ and $\quad c_{s}=\frac{\omega^{0.5}}{\omega \sigma}$
where $\sigma$ is the Warburg impedance obtained from the gradient of appropriate plots of the data using equations (1.24) and (1.25). The rate constant of the reaction, $k_{s}$, can be calculated from:
$\ln \left(\frac{\delta}{1+\exp (-b)}\right)=\ln \left(\frac{k_{s}}{\sqrt{D}}\right)+\alpha b$
where $\alpha$ is the transfer coefficient for the reaction, ${ }^{191} \delta$ and $b$ are obtained from (1.27) and (1.28) respectively
$\delta=\frac{(2 \omega)^{0.5}}{\left(\omega r_{s} c_{s}-1\right)}$
$b=\frac{n F}{R T}\left(\Delta_{o}^{w} \phi-\Delta_{o}^{w} \phi_{1 / 2}\right)$

From equations (1.26) - (1.28), a plot of $\ln \left(\frac{\delta}{1+\exp (-b)}\right)$ versus $b$ will have a slope of $\alpha$ and a y-axis intercept of $\ln \left(k_{s} / D^{1 / 2}\right)$ and from these diagnostic plots all relevant parameters can be calculated. The second order rate constant $k^{0^{\circ}}$ can be obtained from $k_{s}$ as follows:

$$
\begin{equation*}
k_{s}=k^{0^{\prime}}\left(C_{o}\right)^{(1-\alpha)}\left(C_{R}\right)^{\alpha} \tag{1.29}
\end{equation*}
$$

where $C_{O}$ and $C_{R}$ are the concentrations of the oxidised and reduced species.

## 2 Experimental

This Chapter describes the apparatus and the techniques used. The electrochemical cells, electrodes and reagents required for liquid/liquid studies will be discussed.

### 2.1 Instrumentation

The main techniques employed were cyclic voltammetry and Electrochemical Impedance Spectroscopy, EIS. The instrumentation required for voltammetric work is the four-electrode potentiostat. This instrument was also used for the EIS measurements but in two electrode conformation.

### 2.1.1 Four Electrode Potentiostat

A potentiostat ${ }^{192,193}$ is an electrical instrument based on operational amplifiers used to fix the potential of an electrode with respect to a reference. Koryta et al. ${ }^{102,194,195}$ described a four-electrode potentiostat for controlling the electrical potential difference at liquid/liquid interface and Figaszewski et al. ${ }^{196}$ reviewed circuitry for such devices. The four-electrode potentiostat made it possible not only to measure, but also to control the interfacial potential across two immiscible liquids. Ohmic potential drop ( $i R$ drop) is commonly eliminated by the use of a positive feedback loop. ${ }^{197}$ In the present study, an in-house built potentiostat was used. The potential profile was provided using a waveform generator (PP R1 Hi-Tek Instruments, UK) and the output recorded on an $\mathrm{X}-\mathrm{Y}$ chart recorder (Bryans Instruments, UK). Some measurements were also made using an AutoLab PGStat 20 (EcoChemie, NL).

However, the $i R$ compensation of this instrument was unreliable and the current response somewhat noisy.

### 2.1.2 Electrochemical Impedance Spectrometer

For EIS ${ }^{198}$ measurements the sinusoidal potential profile was provided by a frequency response analyser (FRA). In this technique, the real ( $Z^{\prime}$ ) and imaginary ($Z^{\prime}$ ) components of the complex impedance response ( $Z$ ) are measured as a function potential. The AC impedance spectrometer used for these studies, Figure 2.1, utilised a four-electrode potentiostat in a two-electrode configuration, connected to a Solartron 1250 FRA (Solartron, ${ }^{199}$ Farnborough, UK). The FRA was connected via an IEEE interface to a GPIB controller card (PCII 488, National Instruments, Japan) in an IBM compatible Pentium P.C. The software used to control the system was ZPLOT version 1.4 (Scribner Associates, Charlottesville, USA) ${ }^{200}$ under Microsoft Windows 3.11.

### 2.1.3 Instrumentation for Other Techniques

The following instrumentation was employed for non-electrochemical and supporting measurements:

- Conductivity measurements were made with a CDM83 conductivity meter and the conductiometric cell was a CDC104 3 band electrode (both Radiometer Copenhagen, Denmark).
- UV/Visible spectra were obtained using a HP8452A diode array spectrophotometer (Hewlett Packard, USA).
- Atomic absorption spectrophotometry was performed on a PE3110 AAS (Perkin Elmer, USA).
- Ellipsometric measurements were made on an L126B Ellipsometer with a 632.8 nm He-Ne laser (Gaertner Sci. Corp., Chicago IL, USA).
- Transmission electron micrographs of gold nanoparticles were taken on a Philips EM 400 T (Koninklijke Philips Electronics N.V., Eindhoven, The Netherlands).


Figure 2.1 Schematic diagram of the AC impedance equipment

### 2.2 Electrochemical Cells

The cells employed for liquid/liquid experiments vary greatly depending on the task; for voltammetric work a four electrode cell was used, for EIS studies, a two electrode configuration was employed.

### 2.2.1 Four Electrode Cell

The cells used were of a three compartment design and were made of borosilicate glass. The electrodes were in two pairs, with a reference electrode and a counter electrode in each phase. Figure 2.2 shows a photograph and schematic diagram of a typical four electrode cell. The dotted line in the figure represents the position of the interface, $\sigma$, being studied and the dashed line is the organic reference junction. The applied potential corresponds, for example, to the following cell:

$$
\text { SCE } \mid 10 \mathrm{mM} \text { THACl }_{(\mathrm{aq})} \mid 10 \mathrm{mM} \text { THATPBCl }_{(\mathrm{org})}|\sigma| 10 \mathrm{mM} \mathrm{LiCl}_{(\mathrm{aq})} \mid \text { SCE }
$$

0
E
where $\sigma$ represents the interface under investigation. The main advantages of this design are the ease of loading and reproducible interfacial area and volume $( \pm 0.02$ $\mathrm{cm}^{3}$ ) of both the organic and aqueous phases, which allows accurate calculation of concentrations in the cell. The platinum counter electrodes (typically a gauze, wire or foil, $0.5 \mathrm{~cm}^{2}, 99.99 \% \mathrm{Pt}$ ) were sealed directly into the glass walls.


Figure 2.2 Photograph and schematic diagram of a four electrode cell;
a) aqueous phase, b) organic phase, c) organic reference junction, d) organic phase counter electrode, e) aqueous phase counter electrode, f) organic phase reference electrode, g) aqueous phase reference electrode.

The counter electrodes are used to feed the current, whilst the potential difference across the interface is measured between the two reference electrodes. The reference electrodes employed will be discussed later on in this Chapter. The positioning of the reference electrodes with respect to the interface is crucial in liquid/liquid experiments: in the four electrode cells, these are usually placed into compartments terminating in a Luggin capillary situated on either side of the interface. By placing the Luggin close to the interface, the effect of $i R$ drop due to the ohmic resistance of the electrolyte solutions is minimised. $i R$ drop is specially high for organic solutions as the relative permittivity of organic solvents are typically much lower than that of water, thus leading to extensive ion pairing in the organic phase.

### 2.2.2 Two Electrode Cell

For EIS experiments, a two electrode cell was used. This was based on a simplified version of the cell used by Senda et al. ${ }^{40}$ where the reference and counter electrode pair in each phase are replaced by a single electrode. Due to their high intrinsic impedance the Luggin capillaries used in the standard four-electrode cell were eliminated to avoid artefacts.

In EIS experiments, the objective is to observe the change in the cell impedance with applied potential and therefore, the contributions from the cell itself should be minimised. The reference electrodes, such as the SCE, can also contribute to the cell impedance. This will be discussed in Section 2.3.


Figure 2.3 Schematic diagram of the two electrode cell used for EIS measurements

The cell was isolated from external vibrations with a No. 1 anti-vibration pneumatic mount (RS Components, USA). A schematic diagram of the EIS cell is shown in Figure 2.3. Prior to each experiment, the voltammetric response was checked to ensure that the cell set-up was correct as it should be comparable with the response obtained with a four electrode configuration. The voltammetry should display a reversible one electron transfer corresponding to the oxidation and reduction of the organic redox couples used, TCNQ or $\mathrm{Lu}(\mathrm{PC})_{2}$ when the organic solution is in contact with the aqueous ferro/ferricyanide couple.

### 2.2.3 Four Electrode Single Membrane Cell

The cell used for measuring ion transfers reactions across a membrane supported water/1,2-DCE interface is shown in Figure 2.4a. The membranes used for these studies were obtained from cellulose dialysis tubing (Sigma, 43 mm dry width). This was supplied desiccated and flat. Sections of the tubing were cut to length and 3 mm were trimmed from one edge of the flat tube. When the membrane was rehydrated, it readily opened out to give sheets of 80 mm in width. The membrane was sandwiched between the aqueous phase contained in the glass body of the cell and the organic phase in the PTFE section. The interface was a circle of diameter 25 mm . A sketch diagram of the organic compartment is shown in Figure 2.4.b. The cell used for studying ion transfer was:

[^0]
### 2.2.4 Four Electrode Dual Membrane Cell

The cell used to study the voltammetric response of a Supported Liquid Membrane (SLM) is shown in figure 2.4 c . The two aqueous phases, W 1 and W 2 were separated by a membrane supported organic phase. This cell was similar to that described in the previous section. The organic phase was located in a PTFE gasket 6 mm in thickness (Figure 2.4d), sandwiched between two dialysis membranes, 25 mm in diameter. In this case, the potentials refer to the cell:
$\mathrm{Ag} / \mathrm{AgCl}|\mathrm{W} 110 \mathrm{mM} \mathrm{LiCl}|$
membrane $\mid 10 \mathrm{mM}$ THATPBCl| membrane
$|10 \mathrm{mM} \mathrm{LiCl} \mathrm{W} 2| \mathrm{AgCl} / \mathrm{Ag}$

The positioning of the electrodes was also slightly different since no electrodes were present in the organic phase. Reference electrodes were placed in each of the aqueous phases. These were connected to the solution through Luggin capillaries, the tips of which terminated close to the membrane surface. The potential was applied between large area Pt counter electrodes in the two aqueous phases. The W1 phase can be considered as analogous to a "feeder phase" in solvent extraction separations, where the ion of interest would be present, and W2 represents the stripping phase, where the target ion would be concentrated.

### 2.2.5 Four Electrode Dual Membrane Extraction Flow Cell

The extraction flowcell shown in Figure 2.5 was constructed at the Ecole Polyechnique Federal de Lausanne (EPFL). The interface of the flowcell consisted of an array of 8 circular interfaces (each with a radius 1 cm ) giving an interfacial area
of $8 \pi \mathrm{~cm}^{2}$. In constrast with the single interface cells, the EPFL flowcell did not have a well defined cell geometry. The calculation of the volumes of the three main chambers gave values of approximately $32.5 \mathrm{~cm}^{3}$ for each of the aqueous compartments, and approximately $27.5 \mathrm{~cm}^{3}$ for the organic compartment. However, the cell tubing, void volumes and the flexibility of the membranes meant that the volumes required to fill the cell were quite different from the calculated values.

### 2.3 Reference Electrodes

The reference electrodes used for voltammetric experiments were either Saturated Calomel Electrodes (SCE, Radiometer Copenhagen, Denmark) or home made $\mathrm{Ag} / \mathrm{AgCl}$ wire electrodes prepared as described elsewhere. ${ }^{201}$ SCEs cannot be used for EIS work, since these electrodes are purposely manufactured to have a high impedance. When the aqueous supporting electrolyte anion is a halide, e.g. $\mathrm{LiCl}, \mathrm{a}$ high surface area silver/silver halide reference electrode ( $\mathrm{Ag} / \mathrm{AgCl}$ ) can be used. These electrodes give stable potentials, provided that the halide concentration is not too high ( $<1 \mathrm{M}$ ), when the increasing solubility of the silver salt can cause problems. In experiments where $\mathrm{Li}_{2} \mathrm{SO}_{4}$ was used for its salting out characteristics, the $\mathrm{Ag} / \mathrm{AgCl}$ electrode was substituted with a large area platinum gauze and the potential was fixed electrochemically by using a freshly made solution containing an accurately measured ratio of ferro/ferricyanide. The platinum electrodes gave a stable reference potential.


Figure 2.4 a) Single dialysis membrane liquid/liquid cell

b) sketch diagram of single membrane cell organic chamber (not to scale)

c) dual dialysis membrane liquid/liquid cell

d) sketch diagram of dual membrane cell organic chamber (not to scale)


Figure 2.5 Dual membrane dialysis flowcell.

### 2.4 Chemicals

All reagents used were of analytical grade or better unless otherwise stated. The material safety data sheet (MSDS) for each compound was read prior to use and appropriate precautions were taken where necessary. All aqueous solutions were prepared using ultra pure water (MilliQ $18 \mathrm{M} \Omega$ ), and the same standard of water was used for all procedures including washing of organic reagents and final rinsing of glassware.

### 2.4.1 Supporting Electrolytes

### 2.4.1.1 Aqueous Supporting Electrolytes

The base electrolyte concentration in the aqueous compartment was approximately 1 M for electron transfer measurements. There were several reasons for this: if the ferro/ferricyanide concentrations are high, then an even higher concentration of supporting electrolyte must be used, as it is necessary to ensure that the charge is mainly carried by the supporting electrolyte and not by the electroactive species. An additional benefit of the high aqueous supporting electrolyte concentration is the salting out effect of the organic solvent and supporting electrolyte. ${ }^{202-204}$ For ion transfer experiments the aqueous supporting electrolyte concentration was 10 or 50 mM .

Lithium chloride (LiCl, Johnson Matthey Ultrapure 99.99\%), lithium sulfate monohydrate $\left(\mathrm{Li}_{2} \mathrm{SO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}\right.$, Fluka, MicroSelect), tetraphenylarsonium chloride (TPAsCl, Fluka) and tetrahexylammonium chloride (THACl, Fluka) were used without further purification.

### 2.4.1.2 Organic Supporting electrolytes

In order to observe the impedance response of the charge transfer process, the overall cell impedance must be stable and not too large to mask the measurement of the charge transfer process. The dielectric permittivity of the organic solvent is low relative to water and the ionic mobility of the bulky organic ions is lower than the corresponding aqueous ions, and for these reasons, the lower limit of concentration of the organic supporting electrolyte was approximately 10 mM .

For electron transfer studies, the main organic supporting electrolyte was tetraphenylarsonium tetrakis(4-chlorophenyl)borate (TPAsTPBCl) prepared by precipitation from a concentrated aqueous solution of tetraphenylarsonium chloride (TPAsCl, Fluka) and a solution of potassium tetrakis(4-chlorophenyl)borate ( KTPBCl , Fluka) in acetone. The resulting white precipitate was washed with ultra pure water (MilliQ $18 \mathrm{M} \Omega$ ), recrystallised twice from acetone (AnalaR grade, Fisons) and dried under vacuum for 24 hours before use.

For ion transfer work, the supporting electrolytes used were tetrabutylammonium tetraphenylborate (TBATPB, Fluka Puriss), TPAsTPBCl prepared as described previously, tetrahexylammonium tetraphenylborate (THATPB) prepared by the same method as above from their corresponding salts (THACl, Fluka and NaTPB, Fluka), and tetrahexylammonium tetrakis(4-chlorophenyl)borate (THATPBCl) prepared in the same way from THACl and KTPBCl (both Fluka).

CHN microanalyses were performed on the organic supporting electrolytes to confirm purity. Tetrahexylammonium hexafluorophosphate (THAPF ${ }_{6}$, Aldrich) was
also used for some experiments, but the potential window obtained was unsatisfactorily small.

### 2.4.2 Solvents

When choosing an organic solvent for liquid/liquid electrochemical studies several factors must be considered. The major consideration is that the solvent should be immiscible with or have a low solubility in the aqueous phase. As discussed in the Introduction, suitable non-toxic solvents, which can offer a useful polarisation range, are required. Cheng and Schiffrin demonstrated that 2-heptanone and 2-octanone could be used for liquid/liquid electrochemical studies, with 2-octanone providing the greatest potential range. ${ }^{127,128}$

1,2-DCE, (Aldrich Spectrophotometric or HPLC grade 99\%+) was singly distilled before use. All other solvents were used as supplied: acetone (BDH, AnalaR), mesityl oxide (Lancaster Synthesis), MIBK (Spectrophotometric grade, Aldrich), nitrobenzene (Aldrich, 99\%), $m$-nitrotoluene, $o-$ NPOE, $o-$ NPPE, $o-\mathrm{DFB}$ and $m$-DFB (all Fluka). The nitriles, butyronitrile (99+\%), valeronitrile (99.5\%) and octanitrile (heptyl cyanide, 97\%) were all obtained from Aldrich.

### 2.4.3 Other Reagents

$\mathrm{K}_{4} \mathrm{Fe}(\mathrm{CN})_{6}$ and $\mathrm{K}_{3} \mathrm{Fe}(\mathrm{CN})_{6}$ (Fluka puriss), n, n-dimethylaminomethyl ferrocene (CAS number [1271-86-9], Strem Chemicals, USA), tetrakis-hydroxymethylphosphonium chloride (Fluka, pract. $80 \%$ in water) and all platinates (Aldrich) were used as supplied. The tetrahexylammonium salt of $\left[\mathrm{PtCl}_{6}\right]^{2-}$ was prepared by mixing an
excess of THACl dissolved in a minimum of propan-2-ol, with a 20 mM aqueous solution of $\left[\mathrm{PtCl}_{6}\right]^{2-}$. The precipitate formed was vacuum filtered, washed with cold water to remove excess THACl and recrystallised twice from acetone giving bright orange crystals which were soluble in 1,2-DCE. TCNQ (Aldrich 98\%) was recrystallised twice from 1,2-DCE and dried under vacuum for 24 hours before use.

## 3 Electron transfer

### 3.1 Introduction

One of the initial aims of the project was to achieve platinum group metals separations using redox-active ligands. It was hoped that changing the state of charge of appropriate parts of a redox-active ligand would lead to specific complexation and stripping reactions that could be controlled by alternating the redox state of the ligand, thus affording precise electrochemical control of the PGM separations. This was part of an EU project, but regrettably although major features of electron transfer were investigated, the synthetic effort from other laboratories to supply appropriate redox ligands did not produce the required materials.

In the present work, two central issues of electron transfer reactions at liquid/liquid interfaces have been studied. The first, presented in this Chapter, is related to the influence of the concentration of the organic base electrolyte on the measured rate constants. This was important for establishing whether both the thickness of the diffuse double layer in the organic phase and changes in ionic association of the base electrolyte ions affect the values of the rate constant. The second question that has been addressed is to what extent the simple formalisms of electron transfer kinetics are applicable to liquid/liquid interfaces when the dielectric and optical properties of the organic phase are altered. These 'solvent effects' on the rate of electron transfer will be considered in Chapter 4 section 6.

### 3.2 Theory of Electron Transfer at Liquid/Liquid Interfaces

Hush ${ }^{205,206}$ outlined a theory of adiabatic-transfer for outer sphere exchange of electrons between ions in an ionising solvent, applicable to processes where the coordination shell around the ion is not disrupted by the electron transfer process.

One of the fundamental quantities in the theory of electron transfer reactions is the medium or solvent reorganisation free energy, $\lambda_{s}$, defined as the reversible work required to change the solvent polarization from the state which corresponds to the solvent equilibrated to the reactants to the state of the solvent equilibrated with the products of the electron transfer reaction. Marcus was a key worker on this topic making several important contributions in the late 1950 s and early 1960 s. ${ }^{58,207-210} \mathrm{He}$ received the 1992 Nobel Prize for Chemistry ${ }^{59,211}$ "for his contributions to the theory of electron transfer reactions in chemical systems".

Several models have been presented to explain the effect of the medium on the rate of electron transfers between molecular and/or ionic species in solution. Often, the model for the ET process relies on the idea of a dielectric continuum for the solvent surrounding the reactant and products. ${ }^{212}$

The Marcus treatment of electron transfer between species in a single phase considers the solvent reorganisation energy as:

$$
\begin{equation*}
\lambda_{s}=(\Delta e)^{2}\left(\frac{0.5}{a_{1}}+\frac{0.5}{a_{2}}-\frac{1}{R}\right)\left(\frac{1}{n^{2}}+\frac{1}{\varepsilon_{s}}\right) \tag{3.1}
\end{equation*}
$$

where $\Delta e$ is the magnitude of the charge transferred, $R$ is the internuclear distance, $a_{l}$ and $a_{2}$ are the radii of the reactants and $n$ and $\varepsilon_{s}$ are the optical and static dielectric constants respectively. ${ }^{210}$ For a metal electrode,

$$
\begin{equation*}
\lambda_{s}=\frac{(\Delta e)^{2}}{2 a}\left(\frac{1}{n^{2}}+\frac{1}{\varepsilon_{s}}\right) \tag{3.2}
\end{equation*}
$$

where $a$ is now the radius of the reacting species. Marcus ${ }^{213-216}$ and later on, Kharkats ${ }^{217}$ extended this formalism to the case of the interface between two dielectric media and derived an expression for the solvent reorganisation energy. Girault made a comparison of the solvent reorganisation terms of Marcus and Kharkats, it was concluded that the two treatments were in reasonable agreement. ${ }^{218}$

During corrections ${ }^{216}$ to some of his earlier works, Marcus pointed out that the key equations which he had derived were expressions for the second order electron transfer rate constant, $k^{0}$ and for the free energy barrier to reaction, $\Delta G^{\ddagger} .214$

Geblewicz and Schiffrin ${ }^{203}$ had adapted the Nicholson and Shain ${ }^{219,220}$ solution of the diffusion-reaction equation at a metal-liquid interface for use at a liquid/liquid interface. This was achieved by using a large excess of the redox couple in the aqueous phase. The use of a high concentration of the aqueous redox couple $=$. simplifies the rate law from second order to a pseudo-first order rate expression and allowed the application of an one-phase treatment of cyclic voltammetry to a two phase problem.

Marcus analysed the data of Geblewicz and Schiffrin. ${ }^{203}$ It was demonstrated that the pseudo-first order rate constant, $k_{s}$, could be used to calculate the second order rate constant $k^{0}$. This relationship was shown in Equation (1.29).

The reorganisation free energy for electron transfer reactions at liquid/liquid interfaces has also been discussed by Benjamin and Kharkats using electrostatic continuum theory. ${ }^{221}$

### 3.3 Two-Phase Redox Systems

### 3.3.1 Organic Redox Couples

Following the work of Samec, ${ }^{43}$ ET across the liquid/liquid interface was also demonstrated by Geblewicz and Schiffrin, ${ }^{203}$ who observed a quasi-reversible reaction for the lutetium bipthalocyanine/ferro/ferricyanide system. The reaction studied was:

$$
\begin{equation*}
\left[\mathrm{Lu}(\mathrm{PC})_{2}\right]_{(1,2-\mathrm{DCE})}^{+}+\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}^{3-} \leftharpoonup\left[\mathrm{Lu}(\mathrm{PC})_{2}\right]^{2+}{ }_{(1,2-\mathrm{DCE})}+\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}^{4-} \tag{3.3}
\end{equation*}
$$

Seno et al. ${ }^{189}$ used EIS to measure the rate of electron transfer of the same reaction earlier studied by Samec between hexacyanoferrate in the aqueous phase and ferrocene in the organic phase. Cheng and Schiffrin ${ }^{222}$ employed hydrophobic metalloporphyrins as the redox active species in the organic phase and in a subsequent study, used EIS to measure the rate of ET across the water/1,2-DCE interface for three organic redox reagents: $\operatorname{Lu}(\mathrm{PC})_{2}$, ruthenium porphyrin and 7,7',8,8'-tetracyanoquinodimethane (TCNQ).

The separation of electron and ion transfer processes was discussed by Cheng ${ }^{142}$ and Beltran ${ }^{223}$ and later by Cunnane et al. ${ }^{224}$

One of the main difficulties in studying heterogeneous electron transfer reactions in these systems is the possibility of the simultaneous occurrence of electron and ion transfer reactions and for this reason, a strongly hydrophobic organic redox couple is preferred. TCNQ was used in the present work since it is similar to $\mathrm{Lu}(\mathrm{PC})_{2}$ in that it is also hydrophobic. This redox reagent has been employed in spectroelectrochemical studies by Girault et al. ${ }^{225}$ and Dryfe et al. ${ }^{226,227}$ used in situ EPR spectroscopy to follow electron transfer between TCNQ in 1,2-DCE and the ferro/ferricyanide couple in the aqueous phase. The formation of TCNQ radical anions was monitored by following the change in the EPR signal with change in the interfacial potential difference. The decay of the signal when the cell was switched back to open circuit was ascribed to the diffusion of the radicals away from the interface. Solomon and Bard ${ }^{228}$ used SECM to study the same reaction and recently the same couple was investigated using an expanding droplet technique. ${ }^{229}$ Quinn et al. used microholes to study the electron transfer process of several organic couples, including TCNQ, at the water/o-NPOE microinterface. ${ }^{134}$

### 3.3.2 Aqueous Redox Couple

When using the ferro/ferricyanide couple in the aqueous phase, consideration must be given to the possibility that ET to this couple is not entirely reversible. In early studies the reaction was thought to proceed via a simple outer sphere transfer mechanism. However, Peter et al. ${ }^{230}$ observed that varying the supporting electrolyte cation resulted in a change in the rate of ET, the catalytic influence was found to
increase in the order $\mathrm{Li}^{+}<\mathrm{Na}^{+}<\mathrm{K}^{+} \sim \mathrm{Cs}^{+}$. Marecek et al. ${ }^{231}$ proposed that the base electrolyte effect on ferro/ferricyanide ET at gold electrodes was due to a mechanism involving a bridge activated complex.

Beriet and Pletcher ${ }^{232}$ made similar observations for a similar series of cations, the ET rate constant increasing in the order $\mathrm{Li}^{+}<\mathrm{Na}^{+}<\mathrm{K}^{+}<\mathrm{Sr}^{2+}$. They noted that under some conditions, ferricyanide decomposes on the surface of platinum, and some of the reaction products, possibly $\mathrm{CN}^{-}$, block the surface. They attributed the change in the ET kinetics to a change in the extent of this surface blocking, which would arise if the effect of ion-pairing between the ferro/ferricyanide and the electrolyte cation prevented or accelerated the rate of decomposition of the species at the surface.

Kulesza et al. ${ }^{233}$ observed.a similar effect on the rate of ferro/ferricyanide ET at a platinum electrode for a series of anions. At constant sodium salt concentration, the rate of the electrode reaction increased in the order $\mathrm{Br}^{-}>\mathrm{Cl}^{-}>\mathrm{NO}_{3}{ }^{\circ}>\mathrm{PO}_{4}{ }^{3 \cdot}>\mathrm{ClO}_{4}{ }^{-}$ $>\mathrm{CH}_{3} \mathrm{COO}^{-}>\mathrm{SO}_{4}{ }^{2-}>\mathrm{CNS}^{-}>\mathrm{F}$. When LiCl was used as the supporting electrolyte or under acidic conditions a blue colour was observed; this was ascribed to the formation of Prussian Blue (PB). ${ }^{234}$ The concentration of the supporting electrolyte was again found to strongly affect the ET rate constant. ${ }^{234}$

Kinetic and infrared spectroscopic studies by Kitamura et al. ${ }^{235}$ showed that on single crystal platinum electrodes in a $1 \mathrm{mM} \mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ solution, for each of the crystal faces examined, adsorbates were detected, Inukai et al. ${ }^{236}$ had ascribed these to $\mathrm{CN}^{-}$.

The formation of PB on gold electrodes from a weakly acidic solution of ferricyanide ( 0.5 mM ) was measured by Yang et al. ${ }^{237}$ They concluded that the mechanism of PB formation was dependent on the dissociation of ferricyanide ions.

This evidence suggests that the ferro/ferricyanide ET reaction mechanism does not proceed via a simple outer sphere process. However, in the present work the aqueous redox couple was present in great excess to the organic redox couple. Thus, the exact rate of ET in the aqueous phase is not of concern here. The ferro/ferricyanide couple has been used as the aqueous redox component in the presence of $\mathrm{Li}_{2} \mathrm{SO}_{4}$.

By using a high concentration of aqueous supporting electrolyte, the transfer of the TCNQ" radical anion is prevented by salting out. ${ }^{202-204}$ The use of a high supporting electrolyte concentration in the aqueous phase caused the Gibbs energy of transfer of the electrogenerated TCNQ ${ }^{\circ}$ to become very high, thereby separating ET and IT processes sufficiently to enable the observation of an uncoupled ET reaction. It is assumed that by making the redox solution concentrated, the aqueous phase acts as the equivalent of a metal electrode. ${ }^{238}$

### 3.4 Dependence of the Rate Constant on the Organic Base

## Electrolyte Concentration

### 3.4.1 Experimental Details

In previous experiments by Cheng and Schiffrin, ${ }^{222}$ the concentration of the organic supporting electrolyte was 1 mM and the concentration of the electroactive species
used in the case of TCNQ was $50 \mu \mathrm{M}$. In this work concentrations of organic supporting electrolyte in the range 1 to 40 mM were studied to investigate the influence of the base electrolyte concentration on the rate constant. For a 1 mM TPAsTPBCl solution, the impedance response was satisfactory although somewhat noisy; better responses were obtained with 10 mM TPAsTPBCl in 1,2-DCE. This concentration was employed for experiments with other solvents. The ET reaction investigated was:
$\mathrm{TCNQ}_{(\mathrm{org})}+\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}{ }_{(\mathrm{aq})} \leftharpoonup \mathrm{TCNQ}^{-}{ }_{(\mathrm{org})}+\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{3-}{ }_{(\text {aq })}$
$\mathrm{Fe}(\mathrm{II})$ was present in the form of potassium ferrocyanide $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ at a concentration of 0.4 M . In order to fix the redox potential of the aqueous phase the initial concentration of Fe (III) was set at 0.01 M , using $\mathrm{K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$. In order to maximise the potential window, $1 \mathrm{M} \mathrm{Li}_{2} \mathrm{SO}_{4}$ was used as the aqueous supporting electrolyte.

### 3.4.2 Preliminary Results

The organic redox reagent initially used was lutetium biphthalocyanine, $\mathrm{Lu}(\mathrm{PC})_{2}$ $\left[\mathrm{Lu}\left(\mathrm{C}_{32} \mathrm{H}_{16} \mathrm{~N}_{8}\right)_{2}\right]^{+}$at a concentration of $50 \mu \mathrm{M}$. This compound was chosen to test the equipment and the method of analysis since it is stable and very hydrophobic and therefore it does not easily transfer into the aqueous phase. The measured potentials refer to the cell:

$$
\begin{aligned}
& \mathrm{Ag} / \mathrm{AgCl}\left|10 \mathrm{mM} \operatorname{TPAsCl}_{(\mathrm{aq})}\right| 10 \mathrm{mM} \operatorname{TPAsTPBCl}_{(1,2-\mathrm{DCE})}+\mathrm{x} \mathrm{mM} \mathrm{Lu}(\mathrm{PC})_{2(1,2-\mathrm{DCE})} \mid \\
& \sigma\left|1 \mathrm{M} \mathrm{Li}_{2} \mathrm{SO}_{4(\mathrm{aq})}+0.4 \mathrm{M} \mathrm{~K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}+0.01 \mathrm{M} \mathrm{~K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}\right| \mathrm{Pt}
\end{aligned}
$$

Figure 3.1 shows the voltammetric response for electron transfer for $\mathrm{Lu}(\mathrm{PC})_{2}$ in contact with the Fe (II)/(III) aqueous redox system. It can be seen that in the presence of $\mathrm{Lu}(\mathrm{PC})_{2}$ a reversible one electron transfer is present with a peak separation of 62 mV . The voltammetric response is difficult to quantify due to the low solubility of $\mathrm{Lu}(\mathrm{PC})_{2}$ in $1,2-\mathrm{DCE}$. Figure 3.2 shows the sweep rate dependence of the voltammetry showing a large capacitive contribution, $i_{c}$, to the current response. The capacitive current is sweep rate dependent: ${ }^{239}$
$j_{c}=C_{d l} v$
where $C_{d l}$ is the double layer capacitance which can be calculated from :

$$
\begin{equation*}
j / v^{1 / 2}=k+C_{d l} v^{1 / 2} \tag{3.6}
\end{equation*}
$$

An appropriate plot was made (Figure 3.3) and a value of $C_{d l}$ of $16 \mu \mathrm{~F} \mathrm{~cm}^{-2}$ was obtained. The capacitive current was subtracted giving the residual Faradaic current density, $j f$. The data in Figure 3.4 allowed the calculation of the diffusion coefficient of $\mathrm{Lu}(\mathrm{PC})_{2}$ which was found to be $1.45 \times 10^{-6} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$, in reasonable agreement with previous measurements. ${ }^{222}$

Figure 3.5 shows the complex impedance response in the frequency range $0.1-2000$ Hz at different applied potentials in the absence of $\mathrm{Lu}(\mathrm{PC})_{2} . Z$ ' is the real component and $Z^{\prime \prime}$ is the imaginary component of the impedance. This response is similar to that observed by Cheng et al. ${ }^{187}$


Figure 3.1 CV without $i$ compensation of $50 \mu \mathrm{M} \mathrm{Lu}(\mathrm{PC})_{2}$ in 1,2 -DCE in contact with 0.4 M $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}+0.01 \mathrm{M} \mathrm{K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{\text {(q9) }}$, sweep rate $=0.05 \mathrm{~V} \mathrm{~s}^{-1}$.


Figure 3.2 Sweep rate dependence for $50 \mu \mathrm{MLu}(\mathrm{PC})_{2}$ in contact with ferro/ferricyanide with $i R$ compensation.


Figure 3.3 Test of equation (3.6) for the results shown in Figure 3.2.


Figure 3.4 Dependence of the Faradaic current density, $j_{j}$, on the square root of the sweep rate.

Figure 3.6 shows a similar experiment in the presence of $\mathrm{Lu}(\mathrm{PC})_{2}$. As expected, the impedance is decreased by the presence of the organic phase redox couple.

Since the concentration of $\operatorname{Lu}(P C)_{2}$ is limited to $50 \mu \mathrm{M}$ it was decided that TCNQ would be a more convenient ET reagent to use for these studies.

### 3.4.3 TCNQ Results

Electrochemical Impedance Spectroscopy measurements have been made varying the concentration of both the supporting electrolytes and the ET reagent in the cell:

$$
\begin{aligned}
& \mathrm{Ag} / \mathrm{AgCl}\left|x \mathrm{mM} \mathrm{TPAsCl}_{(\mathrm{aq})}\right| x \mathrm{mM} \mathrm{TPAsTPBCl} \\
&(1,2-\mathrm{DCE}) \\
&+y \mathrm{mM} \mathrm{TCNQ} \\
&(1,2-\mathrm{DCE}) \\
& \mid \\
& \quad \sigma\left|0.4 \mathrm{M} \mathrm{~K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}+0.01 \mathrm{M} \mathrm{~K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}+1.0 \mathrm{M} \mathrm{Li}_{2} \mathrm{SO}_{4(\mathrm{aq})}\right| \mathrm{Pt}
\end{aligned}
$$

A baseline cyclic voltammogram is shown in Fig. 3.7 indicating that the electron transfer occurs well within the polarization window. Baseline AC impedance spectra were generally taken at $15 . \mathrm{mV}$ intervals with no electron transfer reagent present. The potential intervals were reduced to 10 mV in the half-wave potential region, in this case, at an applied potential of approximately 300 mV .


Figure 3.5 Complex plane impedance plot in the absence of electron transfer; $\square+0.48 \mathrm{~V}$, +0.57 V and $\mathrm{O}+0.62 \mathrm{~V}$


Figure 3.6 Complex plane impedance plot of $50 \mu \mathrm{M} \mathrm{LuPC}_{2}$ for different applied potentials; $+0.48 \mathrm{~V}, \mathrm{~m}+0.57 \mathrm{~V}$ and $\mathrm{O}+0.62 \mathrm{~V}$

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Figure 3.7 Cyclic voltammogram of (a) baseline and (b) electron transfer following addition of $250 \mu \mathrm{M}$ TCNQ. Sweep rate $=0.05 \mathrm{~V} \mathrm{~s}^{-1}$.


Figure 3.8 Representative cyclic voltammogram of TCNQ electron transfer in a two-electrode cell. Concentration $T C N Q=0.250 \mathrm{mM}$. Sweep rate, $v=0.005,0.010,0.025,0.050,0.075$ and $0.100 \mathrm{~V} \mathrm{~s}^{-1}$.


Figure 3.9 Complex plane impedance plot in the absence (baseline) and presence of TCNQ $(250 \mu \mathrm{M})$ and with the baseline subtracted.


Figure 3.10 Complex plane impedance plot in the presence of $\operatorname{TCNQ}(250 \mu \mathrm{M})$ without baseline subtraction $(\boldsymbol{\diamond})$ and after baseline and solution resistance subtraction ( $\boldsymbol{\square}$ ).

Measurements were performed for different concentrations of supporting electrolyte in the organic phase. The impedance data were processed using the Microsoft Excel 5.0 spreadsheet following the mathematical treatment described by Cheng and Schiffrin. ${ }^{222}$ A sample set of data for 10 mM TPAsTPBCl in $o-D F B$ is included in the Appendix.

The corresponding equations and method of calculation were discussed in Section 1.2.3. Values for $r_{s}$ and $1 / \omega c_{s}$ were calculated from equations (1.22) and (1.23) respectively, plots were made of $r_{s}$ and $1 / \omega c_{s}$ versus $1 / \omega^{0.5}$ in order to extract the values or $R_{c t}$ and $\sigma$ as given by equations (1.24) and (1.25), these plots can be seen in the Appendix in the bottom-right figure for each given potential.

The most important information is given by the dependence of $\ln \{\delta /[1+\exp (-b)]\}$ on the reduced potential $b$, a measure of the difference between applied potential and the half-wave potential of the electron transfer process.

An example of the applicability of eqn. (1.23) is shown in Fig. 3.11. From these plots, the measured rate constants $k_{s}$ and second order rate constants $k^{0^{\prime}}$ were obtained; these were in good agreement with the values obtained previously. ${ }^{222}$ The results obtained are summarised in Table 3.1, which show, that the organic supporting electrolyte concentration does not have a significant effect on the rate of electron transfer across the $1,2-\mathrm{DCE} /$ water interface. This is an important result showing that ion-pairing, that would be important in this solvent, does not influence the activation energy for the reaction. Also it is surprising that diffuse double layer effects do not appear to influence the value of $k_{s}$.


Figure 3.11 Dependence of $\ln \{\delta /[1+\exp (-b)]\}$ on the applied potential for $250 \mu \mathrm{M}$ TCNQ in $1,2-$ DCE. concentration of organic supporting electrolyte $=10 \mathrm{mM}$ TPAsTPBCI.

Table 3.1 Measured rate constants $\left(k_{4}\right)$ and second order rate constants $\left(k^{0^{\prime}}\right)$ as a function of supporting electrolyte concentration.

| [TPAsCl] <br> organic ref. <br> junction / $\mathbf{m M}$ | [TPAsTPBCl] <br> organic phase $/$ <br> $\mathbf{m M}$ | [TCNQ]/ <br> $\mu \mathrm{M}$ | $\mathbf{k}_{\mathbf{s}} /\left(\mathrm{cm} \mathrm{s}^{-1}\right)$ | $\mathbf{k}^{\mathbf{0} /} /\left(\mathrm{cm} \mathrm{s}^{-1}\right.$ <br> $\left.\mathbf{d m}^{\mathbf{3}} \mathrm{mol}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 1 | 50 | $(9.0 \pm 1.1) \times 10^{-3}$ | 0.132 |
| 10 | 10 | 250 | $(3.6 \pm 0.6) \times 10^{-3}$ | 0.128 |
| 10 | 20 | 250 | $(2.4 \pm 0.1) \times 10^{-3}$ | 0.084 |
| 20 | 20 | 250 | $(3.75 \pm 0.7) \times 10^{-3}$ | 0.132 |
| 40 | 40 | 250 | $(3.3 \pm 0.5) \times 10^{-3}$ | 0.098 |

## 4 The Organic Solvent

Liquid/liquid electrochemical studies have traditionally been performed with nitrobenzene (NB) and 1,2-DCE as the organic phase. The toxicity of these solvents was discussed in Section 1.1.8. If liquid/liquid techniques are to be successfully transferred to an industrial scale, less toxic solvents will be required.

### 4.1 Characterisation of Novel Solvents

Initial candidate solvents were the higher and branched ketones, as they have been used in extraction and metal preconcentration studies. ${ }^{169,170}$ Recently Cheng et al. used ketones as solvents for liquid/liquid studies. ${ }^{63,127,128}$ However, their reductive effect on chloroaurate and chloropalladate anions indicate that ketones might be more reactive than at first thought. This problem will be discussed in Chapter 7. There were two possibilities to circumvent this problem:
(i) It is proposed that the reactivity of the ketones is due to a keto-enol tautomerism (Chapter 7). The use of modified ketones such as mesityl oxide, with an additional carbon-carbon double bond, provides conjugation and allows the delocalisation of the $\pi$-electrons away from the $\mathrm{C}=\mathrm{O}$ group. In simple comparative tests, mesityl oxide showed a slightly lower rate of reduction of tetrachloroaurate in comparison to MIBK and octanone. However, the potential window for the mesityl oxide/water system was relatively small, at best 0.2 V , and the results obtained were irreproducible. Voltammetric measurements for the water/ethyl acetate system showed a small potential window of 0.25 V .
(ii) To use a solvent having a different polar group taking into consideration that the dielectric permittivity ( $\varepsilon$ ) must be at least equal to that of $1,2-\mathrm{DCE}$ for the solvent to be of practical use. The solvents considered are shown in Table 4.1. Acetonitrile is widely used for electrochemical studies due to its high relative permittivity, but it is miscible with water and is therefore, unsuitable. The higher nitriles, however, are mostly immiscible with water and offer interesting possibilities. Valeronitrile $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CN}$, butyronitrile $\left(\mathrm{CH}_{2}\right)_{3} \mathrm{CHCN}$ and octanenitrile (heptyl cyanide) have all been considered.
$o$-NPOE was briefly examined as it has a high dielectric permittivity, is highly immiscible with water and is reported to be non-toxic, although on the latter point no toxicity data could be located. Unfortunately, $o$-NPOE has a density of $1.041 \mathrm{~g} \mathrm{~cm}^{-3}$ and although it is immiscible with water, it is somewhat difficult to handle and was deemed to be unsuitable for use in unsupported liquid/liquid interfacial studies. The present work employed instead 2-nitrophenyl pentyl ether (o-NPPE) as it is slightly more dense ( $1.098 \mathrm{~g} \mathrm{~cm}^{-3}$ ) and has only half of the viscosity of $o$-NPOE, making it much more useful for liquid/liquid work. However, o-NPPE is approximately twice as expensive as $o$-NPOE which severely limited the number of voltammetric/EIS experiments that could be carried out. The meta- isomer of nitrotoluene is not as toxic as the ortho-isomer, therefore $m$-nitrotoluene was tested in the present work.

The ortho- and meta- isomers of difluorobenzene ( $o-\mathrm{DFB}$ and $m-\mathrm{DFB}$ ) have been studied in order to make a comparison between similar molecules but having different dipole moments also, a binary mixture of $o-\mathrm{DFB} / 1,2-\mathrm{DCE}$ has been used as the organic solvent to assess the properties of mixtures.

Table 4.1 A summary of useful properties of the solvents examined.

| Solvent | CAS No. | $\mathrm{d}_{4}{ }^{20}$ | $\varepsilon /$ Debye | $\mathrm{n}_{\mathrm{d}}{ }^{20}$ |
| :---: | :---: | :---: | :---: | :---: |
| Water | [7732-18-5] | 1.00 | 78.39 | 1.334 |
| 1,2-DCE | [107-06-2] | 1.256 | 10.2 / 10.42 / 10.45 | 1.444 |
| $o-D F B$ | [367-11-3] | 1.17 | 13.38 | 1.445 |
| $m$-DFB | [372-18-9] | 1.157 | 5.01 | 1.438 |
| 1,2-DCE/m-DFB | - | - | 7.71* | 1.441* |
| Nitrobenzene | [98-95-3] | 1.203 | 35.6/35.96 | 1.552 |
| 3-Nitrotoluene | [99-08-1] | 1.155 | 24.95 | 1.541 |
| 2-Nitrotoluene ${ }^{137}$ | [88-72-2] | 1.163 | 26.26 | 1.544 |
| o-NPPE | [39645-91-5] | 1.098 | 29.15 | 1.522 |
| $o-\mathrm{NPOE}^{134}$ | [37682-29-4] | 1.041 | 24.2/31.78 | 1.511 |
| MIBK | [108-10-1] | 0.800 | 13.1 | 1.396 |
| Butyronitrile | [109-74-0] | 0.791 | - | - |
| Valeronitrile (Pentanenitrile) | [110-59-8] | 0.795 | 24.83 | - |
| Octanonitrile | [124-12-9] | 0.814 | 13.9 | - |

* Average taken from the values for the two component solvents.


### 4.3 The Nitriles

Voltammetric baselines were obtained for the water/valeronitrile, water/butyronitrile and water/octanenitrile interfaces using the cell:
$\mathrm{Ag} / \mathrm{AgCl}\left|10 \mathrm{mM} \operatorname{THACl}_{(\mathrm{aq})}\right| 10 \mathrm{mM} \mathrm{THATPBCl}_{(\mathrm{RCN})}|\sigma| 10 \mathrm{mMLLCl}_{(\mathrm{aq})} \mid \mathrm{AgCl} / \mathrm{Ag}$

The aim here was not to establish an absolute Galvani potential scale using the Grunwald or TPAsTPB assumption, but to screen the solvents to ascertain if a reasonable potential window could be obtained. The nitriles tested gave potential windows in the order of 300 mV using a sweep rate of $20 \mathrm{mV} \mathrm{s}^{-1}$, see Figure 4.1. The largest window was given by butyronitrile at $\sim 340 \mathrm{mV}$.

### 4.2.1 TEA ${ }^{+}$Transfer

To demonstrate that the water/butyronitrile system could be used for simple ion transfer studies, preliminary experiments were conducted for $\mathrm{TEA}^{+}$transfer and the results are shown in Figure 4.2. The half wave potential (applied) $\mathrm{E}_{1 / 2}$ was 321 mV and the peak to peak separation was 66 mV at a sweep rate of $20 \mathrm{mV} \mathrm{s}^{-1}$. The sweep rate dependence for $\mathrm{TEA}^{+}$transfer can been seen in Figure 4.3, and a diffusion coefficient of TEA ${ }^{+}, D_{\text {TEA }}{ }^{+}=2.18 \times 10^{-6} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$ could be calculated from these data and equation (1.13). For the water/valeronitrile system, a transfer wave was observed with $E_{1 / 2}=315 \mathrm{mV}$ (applied potential), and a peak separation of 68 mV at a sweep rate of $20 \mathrm{mV} \mathrm{s}^{-1}$ (Figure 4.4). These results indicate that the higher nitrile solvents, especially butyronitrile, show promise for ion transfer studies.


Figure 4.1 Potential window for the water/valeronitrile, water/butyronitrile and water/octanenitrile interfaces. Sweep rate $=20 \mathrm{mV} \mathrm{s}^{-1}$.


Figure 4.2. TEA ${ }^{+}(435 \mu \mathrm{M})$ transfer at the water / butyronitrile interface. Potential sweep rate of baseline: $20 \mathrm{mV} \mathrm{s}^{-1}$. The sweep rates for the aqueous TEACI were 1,5 and $20 \mathrm{mV} \mathrm{s}^{-1}$.


Figure 4.3 Dependence of the peak current density on $\nu^{1 / 2}$ for $435 \mu \mathrm{M} \mathrm{TEA}^{+}$transfer across the butyronitrile/ water interface.


Figure 4.4 TEA $^{+}(517 \mu \mathrm{M})$ transfer at the water / valeronitrile interface. Sweep rate $=20 \mathrm{mV} \mathrm{s}$. .

### 4.3 The Difluorobenzenes

### 4.3.1 o-Difluorobenzene (o-DFB)

$o$-DFB gave a potential window of over 700 mV , which is comparable to that of $1,2-$ DCE. It is an inert and non-coordinating solvent sometimes used for electrochemical studies of transition metal complexes, ${ }^{241}$ but has not been to our knowledge employed in ITIES studies. o-DFB has similar physical properties to 1,2-DCE, it has a dielectric permittivity of 13.38 and a density of $1.17 \mathrm{~g} \mathrm{~cm}^{-3}$. o-DFB boils at $92^{\circ} \mathrm{C}$ which is $9^{\circ} \mathrm{C}$ higher than 1,2-DCE. It is also less toxic than 1,2-DCE and at $£ 0.32 \mathrm{~g}^{-1}$ is relatively inexpensive when compared to $0-\mathrm{NPOE}$.

Figure 4.5 shows the cyclic voltammetry of TCNQ in $o-\mathrm{DFB}$, the cell used was:
$\operatorname{SCE}\left|10 \mathrm{mM} \operatorname{TPAsCl}_{(\mathrm{aq})}\right| 2 \mathrm{mM} \operatorname{TPAsTPBCl}_{(0)}|\sigma|$

$$
0.4 \mathrm{M} \mathrm{~K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}+0.01 \mathrm{M} \mathrm{~K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}+1.0 \mathrm{M} \mathrm{Li}_{2} \mathrm{SO}_{4(\mathrm{aq})} \mid \mathrm{SCE}
$$

The potential quoted is the applied potential. The baseline shows a potential window of over 0.6 V. Aliquots of a stock solution of TCNQ in o-DFB were pipetted into the organic phase and the current increased accordingly. A sweep rate dependence was carried out following subtraction for the capacitive current in the baseline using the method described by Kontturi et al. ${ }^{242}$ From the gradient of the faradaic current plot in Figure 4.6, a value for the diffusion coefficient of TCNQ in $o-D F B$ was obtained, where $\mathrm{D}_{\mathrm{TCNQ}}=2.4 \times 10^{-6} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$.


Figure 4.5 Cyclic voltammogram of TCNQ electron transfer across the water / o-DFB interface with increasing concentration, sweep rate $=0.050 \mathrm{~V} \mathrm{~s}^{-1}$.


Figure 4.6 Sweep rate dependence of peak current density for $250 \mu \mathrm{M}$ TCNQ electron transfer across the water / 0 -DFB interface.

### 4.3.2 $m$-Difluorobenzene ( $m$-DFB)

Table 4.1 shows the difference in dielectric permittivity between the two isomers of difluorobenzene. The $m$-DFB isomer has the obvious disadvantage of a low dielectric permittivity, which results in a low solubility of the organic supporting electrolyte in this solvent. The maximum concentration of TPAsTPBCl which would dissolve in $m-\mathrm{DFB}$ at room temperature was 1.5 mM . For this reason, mixtures of $m-\mathrm{DFB}$ and 1,2-DCE were investigated.

It was found that the supporting electrolyte could be dissolved at higher concentrations. However, the potential window obtained by cyclic voltammetry varied with the ratio of the two solvents. In order to make a comparison between the binary solvent mixtures and the pure solvents, it was decided to test the electrochemical response for different ratios of $m$-DFB to $1,2-\mathrm{DCE}$. The cell used for this series of experiments was:
$\mathrm{Ag} / \mathrm{AgCl}\left|10 \mathrm{mM} \operatorname{TPAsCl}_{(\mathrm{aq})}\right| 1.5 \mathrm{mM} \operatorname{TPAsTPBCl}_{(\mathrm{o})}|\sigma| 10 \mathrm{mM} \mathrm{LiCl}_{(\mathrm{aq})} \mid \mathrm{Ag} / \mathrm{AgCl}$

The sweep rate used for comparing these solvents was $5 \mathrm{mV} \mathrm{s}^{-1}$. The results are shown in Table 4.2 and Figure 4.7. The limit at the positive end of the potential window is due to the transfer of $\mathrm{Li}^{+}$from the aqueous to the organic phase, or the transfer of $\mathrm{TPBCl}^{-}$in the opposite direction.

Table 4.2 Properties of Mixtures of $m$-DFB and 1,2-DCE

| $\%$ m-DFB | \% 1,2-DCE | Potential limits / mV |
| :---: | :---: | :---: |
| 100 | 0 | $130-750$ |
| 92 | 8 | $155-760$ |
| 80 | 20 | $155-760$ |
| 66 | 34 | $155-825$ |
| 50 | 57.5 | $155-840$ |
| 42.5 | 62 | $155-860$ |
| 38 | 66 | $155-805 \star$ |
| 34 | 73 | $155-850$ |
| 20 | 80 | $155-880$ |
| 0 | 100 | $155-885$ |



Figure 4.7 Dependence of the positive potential limit on the ratio of $\boldsymbol{m}$-DFB : 1,2-DCE.

Various standard electrochemical experiments were conducted in the binary mixtures, including TEA ${ }^{+}$ion transfer, chloroplatinate ion transfer, and TCNQ electron transfer experiments (Figure 4.8) all of which gave reasonable, reversible electrochemistry.

### 4.4 3-Nitrotoluene

3-Nitrotoluene with a dielectric permittivity of 13.38 and a density of $1.17 \mathrm{~g} \mathrm{~cm}^{-3}$ has similar physical properties to nitrobenzene which is to be expected as it is a congener. Whilst toxic by inhalation, it is not a suspected carcinogen and is relatively inexpensive at $£ 0.03$ per $\mathrm{cm}^{3}$. 3-Nitrotoluene gave a potential window of several hundred mV which was comparable with some of the ketones investigated.

Figure 4.9 shows a baseline for the cell configuration:
$\mathrm{Ag} / \mathrm{AgCl}\left|10 \mathrm{mM} \mathrm{TPAsCl} \mathrm{l}_{(\mathrm{aq})}\right| 10 \mathrm{mM} \operatorname{TPAsTPBCl} \mathrm{l}_{(0)}|\sigma|$

$$
10 \mathrm{mM} \mathrm{~K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}+1 \mathrm{mM} \mathrm{~K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}+10 \mathrm{mM} \mathrm{Li}_{2} \mathrm{SO}_{4(\mathrm{aq})} \mid \mathrm{Pt}
$$

The addition of TCNQ yielded an increase in the current at the far edge of the potential window, but this was masked by transfer of the supporting electrolyte. Also the low concentration of the supporting electrolyte in the aqueous phase can be improved on, by using higher concentrations of $\mathrm{Li}_{2} \mathrm{SO}_{4}$ it was possible to extend the potential window.


Figure 4.8 Cyclic voltammogram of TCNQ electron transfer across the water / (m-DFB / 1,2DCE) interface.


Figure 4.9 Cyclic voltammogram of $100 \mu \mathrm{M}$ TCNQ in 3-Nitrotoluene.

### 4.5 Methyl Isobutyl Ketone (MIBK)

The use of MIBK as a solvent for liquid/liquid studies and solvent extraction was discussed in section 1.1.8. MIBK was previously been employed for selective solvent extraction of platinum, using dithizone ${ }^{243}$ as a complexing agent. In Chapter 5 the ion transfer of tetra- and hexachloroplatinate across the water/MIBK interface will be reported.

### 4.6 Dependence of the Rate Constant on the Solvent

The influence of the solvent on the rate constants of electron transfer can be analyzed from the point of view of its contribution to the solvent reorganisation energy. This is an important issue in the theory of ET at liquid/liquid interfaces and for this reason a group of solvents showing a wide range of dielectric permittivities were chosen.

The redox system studied was the same as that discussed in section 3.4 , since its kinetics are now well known. The experimental approach was identical to that described in Chapter 3 the cell used was as follows:

$$
\begin{aligned}
& \mathrm{Ag} / \mathrm{AgCl} \mid 10 \mathrm{mM} \mathrm{TPAsCl}_{(\mathrm{aq})} \mid 10 \mathrm{mM} \mathrm{TPAsTPBCl} \\
&(\mathrm{org}) \\
&+0.250 \mathrm{mM} \mathrm{TCNQ}_{(\mathrm{org})} \mid \\
& \quad \sigma\left|0.4 \mathrm{M} \mathrm{~K}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}+0.01 \mathrm{M} \mathrm{~K}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{(\mathrm{aq})}+1.0 \mathrm{M} \mathrm{Li}_{2} \mathrm{SO}_{4(\mathrm{aq})}\right| \mathrm{Pt}
\end{aligned}
$$

and the results obtained are summarized in Table 4.3. If the solvent makes an important contribution to the reorganisation energy, the Marcusian term

$$
\begin{equation*}
B=\left(\frac{1}{n^{2}}+\frac{1}{\varepsilon_{s}}\right) \tag{3.7}
\end{equation*}
$$

should be the variable that determines the rate constant. Tables 4.3 and 4.4 collect all the data and Figure 4.10 shows this dependence.

Surprisingly, the Marcusian term does not determine value of the rate. This is an unusual result, which indicates that factors other than solvent polarization must play an important role in ET kinetics at liquid/liquid interfaces.


Figure 4.10 Dependence of the rate constant for electron transfer on the Marcusian term B for the different solvents investigated.

Table 4.3 Measured rate constants $\left(k_{s}\right)$ and second order rate constants $\left(k^{0}\right)$ for some solvents.

| Solvent | $\mathbf{k}_{\mathbf{s}} /\left(\mathrm{cm} \mathrm{s}^{-1}\right)$ | $\alpha$ | $\mathbf{D} /\left(\mathrm{cm}^{2} \mathbf{s}^{-1}\right)$ | $\mathbf{k}^{\mathbf{0}} /\left(\mathrm{cm} \mathrm{s}^{-1} \mathbf{d m}^{\mathbf{3}} \mathrm{mol}^{-1}\right)$ |
| :--- | :---: | :---: | :---: | :---: |
| 1,2-DCE | $5.4 \times 10^{-3}$ | 0.33 | $8.9 \times 10^{-6}$ | $1.29 \times 10^{-1}$ |
| o-NPPE | $4.1 \times 10^{-3}$ | 0.42 | $2.6 \times 10^{-7}$ | $3.25 \times 10^{-1}$ |
| o-DFB | $4.4 \times 10^{-4}$ | 0.33 | $2.4 \times 10^{-6}$ | $1.32 \times 10^{-3}$ |
| 3-Nitrotoluene | $8.8 \times 10^{-4}$ | 0.16 | $1.45 \times 10^{-5}$ | $3.33 \times 10^{-1}$ |
| Nitrobenzene | $3.2 \times 10^{-4}$ | 0.61 | $4.7 \times 10^{-6}$ | $8.37 \times 10^{-2}$ |
| $m$-DFB/1,2-DCE | $2.3 \times 10^{-4}$ | 0.42 | $6.1 \times 10^{-8}$ | $1.92 \times 10^{-2}$ |

Table 4.4 Summary of the values and physical properties required for the calculation of permittivity effects on the value of the rate constant.

| Solvent | Refractive <br> index (n) | Dielectric <br> Permittivity ( $\varepsilon)$ | $\mathbf{B = ( 1 / \mathbf { n } ^ { 2 } - 1 / \varepsilon )}$ |
| :--- | :---: | :---: | :---: |
| 1,2-DCE | 1.444 | 10.42 | 0.384 |
| o-NPPE | 1.522 | 29.15 | 0.397 |
| 1,2-DFB | 1.445 | 13.38 | 0.404 |
| 3-Nitrotoluene | 1.544 | 24.95 | 0.379 |
| Nitrobenzene | 1.552 | 35.7 | 0.387 |
| $m$-DFB /1,2-DCE* | 1.441 | 7.71 | 0.352 |

## 5 Ion Transfer

The standard Galvani transfer potential of an ion from phase $\alpha$ to phase $\beta, \Delta_{\beta}^{\alpha} \phi_{i}^{o}$, is related to the standard Gibbs energy of transfer of the ion, $\Delta G_{t, i}^{o, \alpha \rightarrow \beta}$ by:

$$
\begin{equation*}
\Delta_{\beta}^{\alpha} \phi_{i}^{o}=\Delta G_{t, i}^{o, \alpha \rightarrow \beta} / z_{i} F \tag{5.1}
\end{equation*}
$$

The usual electrochemical methodology for the study of electrode reactions can be used for ion transfers across the liquid/liquid interface. The formal transfer potential, $\Delta_{\beta}^{\alpha} \phi_{i}^{o}$, can be measured using cyclic voltammetry in the same manner used to measure the formal redox potential of a species at a solid electrode. The formal transfer potential includes the activity coefficients of the ions in the contacting phases and is related to the apparent standard potential through:

$$
\begin{equation*}
\Delta_{\beta}^{\alpha} \phi_{l}^{o}=\Delta_{\beta}^{\alpha} \phi_{l}^{o}+\frac{R T}{z_{i} F} \ln \left(\frac{\gamma_{i}^{\beta}}{\gamma_{i}^{\alpha}}\right) \tag{5.2}
\end{equation*}
$$

where $\gamma_{l}^{\alpha}$ and $\gamma_{l}^{\beta}$ are the activities of the transferring species. The formal transfer potential is calculated from the apparent Gibbs energy of transfer $\Delta G_{t, i}^{o, \alpha \rightarrow \beta}$ from (5.1). The systems under consideration are unusual in that the metal ions are present as anions: gold as tetrachloroaurate, $\left[\mathrm{AuCl}_{4}\right]^{-}$, and platinum as tetra- or hexachloroplatinate, $\left[\mathrm{PtCl}_{4}\right]^{2-}$ and $\left[\mathrm{PtCl}_{6}\right]^{2-}$ respectively. Cheng et al. ${ }^{244}$ reported that chloroplatinate anions are amenable to simple ion transfer at the water/1,2-DCE and water/MIBK interfaces.

Also, it was reported that there is an appreciable difference in the transfer potential between tetrachloroplatinate $\left[\mathrm{PtCl}_{4}\right]^{2-}$ and hexachloroplatinate $\left[\mathrm{PtCl}_{6}\right]^{2-}$. This may be attributed to the difference in geometry as the former is a square planar and the latter an octahedral complex.

## 5.1 $\mathrm{Pt}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{IV})$ Simple Ion Transfers

In order to study the factors contributing to the transfer potential of PGM complexes into the organic phase with a view to developing a selective ligand separation strategy, it was decided to study a series of simple charged platinum complexes with different ligands. The cell used for this series of experiments was of the form:
$\operatorname{SCE}\left|10 \mathrm{mM} \mathrm{THACl}_{(\mathrm{aq})}\right| 10 \mathrm{mM}$ THATPBCl $_{\text {(org) }}$

$$
|\sigma| 10 \mathrm{mM} \mathrm{LiCl}_{(\mathrm{aq})}+\mathrm{x} \mathrm{mM}\left[\mathrm{PtX}_{4 / 6}\right]^{2-} \mid \mathrm{SCE}
$$

Figure 5.1 shows a typical cyclic voltammogram for platinate anion transfer, from water to $1,2-\mathrm{DCE}$. The results for nearly all the other complexes studied were very similar. The transfer reaction is diffusionally controlled as shown for $\left[\mathrm{PtCl}_{6}\right]^{2-}$ in Figure 5.2 and for $\left[\mathrm{PtCl}_{4}\right]^{2-}$ in Figure 5.3. A summary of the results obtained is given in Table 5.1.

The peak to peak separation for most of the complexes was in the range of 30-35 mV , which corresponds to the transfer of a doubly charged species. This is in keeping with the two charges carried by the platinate ions.


Figure 5.1 Cyclic voltammogram of $157 \mu \mathrm{M}\left[\mathrm{PtCl}_{6}\right]^{2-}$ ion transfer across the water/1,2-DCE interface at different sweep rates. The complex was present as hexachloroplatinic acid.


Figure 5.2 Dependence of the peak current density on sweep rate for the transfer of $157 \mu \mathrm{M}$ $\left[\mathrm{PtCl}_{6}\right]^{2-}$ across the water/1,2-DCE interface.


Figure 5.3 Dependence of the peak current density on sweep rate for the transfer of $70 \mu \mathrm{M}$ $\left[\mathrm{PtCl}_{4}\right]^{2-}$ across the water/1,2-DCE interface.

Table 5.1 Summary of Galvani potential, reversibility and number of charges involved in the transfer of $\mathrm{Pt}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{IV})$ complexes across the water/1,2-DCE interface.

| Complex | Rev/irr, n | $\mathrm{E}_{1 / 2} / \mathrm{mV}$ | $\Delta_{0}^{\prime \prime \prime} \phi / \mathrm{V}$ | $\Delta G_{\text {transer }}^{0} \boldsymbol{0}$, $/ \mathbf{k J ~ m o l}{ }^{-1}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\left(\mathrm{NH}_{4}\right)_{2}\left[\mathrm{PtCl}_{4}\right]$ | Reversible, $\mathrm{n}=2$ | 186 | -0.286 | -55.2 |
| $\mathrm{H}_{2}\left[\mathrm{PtCl}_{6}\right] \cdot \mathrm{xH} \mathrm{H}_{2} \mathrm{O}$ | Reversible, $\mathrm{n}=2$ | 288 | -0.184 | -35.5 |
| $\mathrm{K}_{2}\left[\mathrm{PtBr}_{6}\right]$ | Reversible, $\mathrm{n}=2$ | 221 | -0.251 | -48.4 |
| $\mathrm{K}_{2}\left[\mathrm{PtCl}_{6}\right]$ | Reversible, $\mathrm{n}=2$ | 292 | -0.180 | -34.7 |
| $\mathrm{K}_{2}\left[\mathrm{Pt}(\mathrm{CN})_{6}\right]$ | Reversible, $\mathrm{n}=2$ | 320 | -0.152 | -29.3 |
| $\mathrm{K}_{2}\left[\mathrm{PtI}_{6}\right]$ | irr, $\mathrm{n}=2$ | 405 | -0.067 | -12.9 |
| $\mathrm{K}_{2}\left[\mathrm{PtBr}_{4}\right]$ | Reversible, $\mathrm{n}=2$ | 157 | -0.315 | -60.8 |
| $\mathrm{K}_{2}\left[\mathrm{PtCl}_{4}\right]$ | Reversible, $\mathrm{n}=2$ | 182 | -0.290 | -56.0 |
| $\mathrm{K}_{2}\left[\mathrm{Pt}(\mathrm{CN})_{4}\right]$ | Reversible, $\mathrm{n}=2$ | 185 | -0.287 | -55.4 |
| $\mathrm{K}_{2}\left[\mathrm{Pt}\left(\mathrm{NO}_{2}\right)_{4}\right]$ | Reversible, $\mathrm{n}=1$ | 281 | -0.191 | -36.9 |
| $\mathrm{Na}_{2}\left[\mathrm{PtCl}_{4}\right] \cdot \mathrm{xH}_{2} \mathrm{O}$ | Reversible, $\mathrm{n}=2$ | 181 | -0.291 | -56.2 |
| $\left(\mathrm{NBu}_{4}\right)_{2}\left[\mathrm{PtCl}_{6}\right]$ | irr, $\mathrm{n}=2$ | 266 | -0.206 | -39.8 |

The transfer peak current for $\left[\mathrm{PtI}_{6}\right]^{2-}$ diminished during the course of the experiment. $\mathrm{Pt}(\mathrm{IV})$ complexes are generally kinetically inert, therefore ligand exchange of iodide with water is likely to procede very slowly. The solution was seen to turn black, which must be due to the liberation of iodine, possibly due to a light catalysed decomposition reaction, where the $\mathrm{Pt}(\mathrm{IV})$ was reduced to $\mathrm{Pt}(\mathrm{II})$ and $\mathrm{I}_{2}$ liberated:
$\left[\mathrm{PtI}_{6}\right]_{(\mathrm{aq})} \xrightarrow{\mathrm{hv}}\left[\mathrm{PtI}_{4}\right]^{2-}{ }_{(\mathrm{aq})}+\mathrm{I}_{2}$

It is likely that $\left[\mathrm{PtI}_{4}\right]^{2-}$ will have a different Gibbs energy of transfer to $\left[\mathrm{PtI}_{6}\right]^{2-}$ which would result in a decrease in the current due to $\left[\mathrm{PtI}_{6}\right]^{2-}$ transfer. Also, an increase in peak separation was observed during the course of the experiment, perhaps due to the presence of mixtures of anions of different charge such as $\operatorname{PtI}_{6}{ }^{2-}$ and $\left[\mathrm{PtI}_{5}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{-}$.

The tetranitroplatinate $\mathrm{K}_{2} \mathrm{Pt}\left(\mathrm{NO}_{2}\right)_{4}$ complex gave a reversible single charge transfer voltammetric wave. It is possible that the tetranitroplatinate anion forms an ion pair with either $\mathrm{THA}^{+}$in the organic phase or $\mathrm{Li}^{+}$at the interface. This was not investigated further.

In building a relationship between the nature and geometry of the ligands and the transfer potential, a first consideration is that any given $\mathrm{Pt}(\mathrm{II})$ complex will transfer at a more negative Galvani potential than its $\mathrm{Pt}(\mathrm{IV})$ analogue. It is proposed that this difference is due to the square planar geometry of $\mathrm{Pt}(\mathrm{II})$ compared with the octahedral geometry of $\mathrm{Pt}(\mathrm{IV})$.

The geometry of the complex governs the positioning of ligands around the ion and therefore has a strong effect on the solvent accessible surface of the ion.

Traditional treatment of the Gibbs energy of transfer of metal ions across a liquid/liquid interface has been based on Born-type electrostatic solvation model, where the ion is considered a hard sphere of a given radius $r$. Osakai et al. ${ }^{245}$ proposed a model for the transfer of a hydrophilic hydrated polyanion into the organic phase taking into account the ionisation potential of the surface atoms of the ion and the electron affinity of the solvent, however the shape of the polyanion was still spherical. In the case of $\left[\mathrm{Pt}(\mathrm{CN})_{4}\right]^{2-}$ the shape of the complex is far removed from a hard sphere and so it may be solvated in a different manner to the octahedral $\left[\mathrm{Pt}(\mathrm{CN})_{6}\right]^{2-}$ complex, which is more similar in shape to a sphere. This will be discussed further in section 5.6.

Diffusion coefficients were calculated from equation (1.13) and are presented in Table 5.2. The diffusion coefficient for a spherical molecule or ion can be calculated using the Stokes-Einstein equation ${ }^{86}$ (5.4):
$D^{0}=\frac{k T}{6 \pi \eta r}$
where $k$ is Boltzmann's constant, $T$ is the temperature, $\eta$ is the viscosity of the solvent and $r$ is the radius of the ion. The calculated diffusion coefficients, $D_{\text {calc }}$, for the hexa- cyano-, chloro- and bromoplatinates are presented alongside the measured diffusion coefficients in Table 5.2. Although the agreement between the measured and the calculated diffusion coefficients was not as good as might be hoped, it is
noted that the calculated values are in the same order with the hexacyano-diffusing fastest and the hexabromoplatinate the slowest of the three.

The values of $D_{\text {calc }}$ for the square planar $\mathrm{Pt}(\mathrm{II})$ ions are not presented due to the nonspherical geometry of the square planar structure. The Stokes-Einstein equation can be adapted to estimate the diffusion coefficient of an oblate sphere, ${ }^{246}$ where the axial ratio of the molecule is taken into account, unfortunately these values were not available for the ions studied.

The results in Table 5.1 show that by varying the ligand and the oxidation state of Pt , the value of $\Delta_{o}^{w} \phi$ can be varied by up to 250 mV . The chloride, bromide and cyanide complexes of both $\mathrm{Pt}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{IV})$ were examined and the results are shown in Table 5.3. It is interesting to note that the difference in half-wave potential between $\mathrm{Pt}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{IV}), \delta \Delta E_{1 / 2}$, was not constant.

Figure 5.4 shows that when equimolar amounts of $\left[\mathrm{Pt}(\mathrm{CN})_{4}\right]^{2-}$ and $\left[\mathrm{Pt}(\mathrm{CN})_{6}\right]^{2-}$ are present, the two transfer waves are well separated. A similar experiment with tetraand hexabromoplatinate, (Fig. 5.5) again two waves were observed, however, they were not as clearly separated as for the cyanoplatinates, this was in keeping with the results presented in Table 5.1. This demonstrates that a mixed solution of $\mathrm{Pt}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{IV})$ could be separated by control of the interfacial potential.

Table 5.2 A summary of diffusion coefficients obtained experimentally $D_{\text {exp }}$ and by calculation from the Stokes-Einstein equation, $\boldsymbol{D}_{\text {calc }}$ for a series of platinate anions.

| Platinate | $\boldsymbol{D}_{\text {exp }} / \mathrm{cm}^{2} \mathrm{~s}^{-1}$ | Ionic Radius $/ \mathrm{m}$ | $D_{\text {calc }} / \mathrm{cm}^{2} \mathrm{~s}^{-1}$ |
| :---: | :---: | :---: | :---: |
| $\left[\mathrm{Pt}(\mathrm{CN})_{6}\right]^{2-}$ | $8.8 \times 10^{-6}$ | $3.70 \times 10^{-10}$ | $6.64 \times 10^{-6}$ |
| $\left[\mathrm{PtCl}_{6}\right]^{2-}$ | $4.7 \times 10^{-6}$ | $4.13 \times 10^{-10}$ | $5.95 \times 10^{-6}$ |
| $\left[\mathrm{PtBr}_{6}\right]^{2-}$ | $4.5 \times 10^{-6}$ | $4.41 \times 10^{-10}$ | $5.56 \times 10^{-6}$ |
| $\left[\mathrm{Ptt}_{4} \mathrm{CN}_{4}\right]^{2-}$ | $5.3 \times 10^{-6}$ | $3.68 \times 10^{-10}$ | - |
| $\left[\mathrm{PtCl}_{4}\right]^{2-}$ | $8.9 \times 10^{-6}$ | $4.11 \times 10^{-10}$ | - |

Table 5.3 A comparison of the Galvani potential of transfer by $\mathrm{Pt}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{IV})$ oxidation state.

| Pt(II) complex | $\Delta_{0}^{\mathrm{w}} \mathrm{\phi} / \mathrm{Volts}$ | Pt(IV) complex | $\Delta_{0}^{\text {w }}$ / / Volts | $\delta \Delta_{0}^{\text {w }} \phi /$ Volts |
| :---: | :---: | :---: | :---: | :---: |
| $\left[\mathrm{PtCl}_{4}\right]^{2-}$ | -0.290 | $\left[\mathrm{PtCl}_{6}\right]^{2-}$ | -0.180 | 0.110 |
| $\left[\mathrm{PtBr}_{4}\right]^{\text {2 }}$ | -0.315 | $\left[\mathrm{PtBr}_{6}\right]^{2-}$ | -0.251 | 0.064 |
| - | - | $\left[\mathrm{PtI}_{6}\right]^{2-}$ | -0.067 | - |
| $\left[\mathrm{Pt}(\mathrm{CN})_{4}\right]^{2-}$ | -0.287 | $\left[\mathrm{Pt}(\mathrm{CN})_{6}\right]^{2-}$ | -0.152 | 0.135 |
| $\left[\mathrm{Pt}\left(\mathrm{NO}_{2}\right)_{4}\right]^{2-}$ | -0.191 | - | - | - |



Figure 5.4 Cyclic voltammogram of (a) baseline and (b) $43 \mu \mathrm{M}\left[\mathrm{Pt}(\mathrm{CN})_{4}\right]^{2-}+43 \mu \mathrm{M}\left[\mathrm{Pt}(\mathrm{CN})_{6}\right]^{2-}$


Figure 5.5 Cyclic voltammogram of (a) baseline and (b) $42 \mu \mathrm{M}\left[\mathrm{PtBr}_{4}\right]^{2-}+42 \mu \mathrm{M}\left[\mathrm{PtBr}_{6}\right]^{2-}$

The counter cation seems to have little effect on the transfer potentials of the platinates with the exception of the tetrabutylammonium salt of $\left[\mathrm{PtCl}_{6}\right]^{2-}$. The three $\left[\mathrm{PtCl}_{4}\right]^{2-}$ complexes examined gave transfer potentials which were in good agreement, the largest difference being only 5 mV and falling within experimental error. The transfer potentials of the potassium salt of $\left[\mathrm{PtCl}_{6}\right]^{2-}$ and hexachloroplatinic acid were in good agreement, again within experimental error.

From Table 5.1, the difference in the transfer potentials of the tetrabutylammonium salt $\left(\mathrm{NBu}_{4}\right)_{2}\left[\mathrm{PtCl}_{6}\right], \Delta_{o}^{\omega} \phi=-0.206 \mathrm{~V}$, and the potassium salt and the acid, $\Delta_{o}^{\omega} \phi=-0.180$ V and -0.184 V respectively, was of the order of $20-25 \mathrm{mV} .\left(\mathrm{NBu}_{4}\right)_{2}\left[\mathrm{PtCl}_{6}\right]$ was not soluble in water and was added to the organic phase. Due to the nature of the counter cation, it is possible that this complex did not fully dissociate in 1,2-DCE and therefore a different half wave potential might be expected.

As mentioned in Chapter 1, Yamamoto and Katoh ${ }^{167}$ examined the distribution behaviour of hexachloroplatinate with quaternary ammonium cations across the water/chloroform and water/carbon tetrachloride interfaces. They proposed that the complex which partitioned to the organic phase was a neutral salt formed in the aqueous phase:

$$
\begin{equation*}
\left[\mathrm{PtCl}_{6}\right]_{(\mathrm{aq})}^{2-}+2\left(\mathrm{NR}_{4}\right)^{+}{ }_{(\mathrm{aq})} \leftharpoonup\left(\mathrm{NR}_{4}\right)_{2}\left[\mathrm{PtCl}_{6}\right]_{(\mathrm{org})} \tag{5.5}
\end{equation*}
$$

In order to further test this assumption and to investigate the cation effect described above, the conductivity of solutions of the tetrahexylammonium salt of hexachloroplatinate was measured. The aim of the conductivity measurements was
to determine the association constant of $(\mathrm{THA})_{2}\left[\mathrm{PtCl}_{6}\right]$ in $1,2-\mathrm{DCE}$, which is important for evaluating the degree of ion pairing between $\left[\mathrm{PtCl}_{6}\right]^{2-}$ in the aqueous phase and the supporting electrolyte cation. A similar study was made by Kontturi et al., ${ }^{247}$ who observed that the positive polarisation limit for the transfer of $\mathrm{Rb}^{+}$was shifted by 200 mV when changing the organic base electrolyte anion from TPB to TPBCl . In order to test the assumption that the shift in transfer potential was due to an ion-pairing effect, these authors measured the dissociation constants for two rubidium salts: rubidium tetraphenylborate ( RbTPB ) and rubidium tetrakis-4chlorophenylborate ( RbTPBCl ).

Using Bjerrum's theory of ion-pair formation, the distance of closest approach, $b$, can be obtained from values tabulated against the definite integral $Q(b)^{248}$ :

$$
\begin{equation*}
Q=\frac{\left|z_{1} z_{2}\right| e^{2}}{2 \varepsilon K^{-1} T} \tag{5.6}
\end{equation*}
$$

For the present case, it is possible that the platinate anions form an ion pair with the supporting electrolyte cation. Tetrahexylammonium was chosen as the counter cation since it was used as the organic phase supporting electrolyte cation for the ion transfer experiments due to its hydrophobic nature and the large value of $\Delta G_{\text {Trans }}^{0 \rightarrow \boldsymbol{*}}$. Since $\left[\mathrm{PtCl}_{6}\right]^{2-}$ is doubly charged, it is expected that it will be mainly present as the singly charged ion pair $\left[\mathrm{THA}\left(\mathrm{PtCl}_{6}\right)\right]^{-}$and the dissociation equilibrium that needs to be considered is:

$$
\begin{equation*}
\left[\mathrm{THA}_{2}\left(\mathrm{PtCl}_{6}\right)\right] \leftharpoonup\left[\mathrm{THA}\left(\mathrm{PtCl}_{6}\right)\right]^{-}+\mathrm{THA}^{+} \tag{5.7}
\end{equation*}
$$

Following the treatment of Fuoss, ${ }^{248,249}$ for a 1:1 electrolyte and ignoring as a first approximation the activity coefficient correction, the conductivity depends on the concentration through:

$$
\begin{equation*}
\Lambda=\sqrt{\frac{K}{c}} \Lambda^{0} \tag{5.8}
\end{equation*}
$$

Figure 5.6 shows the concentration dependence of the conductivity of $\mathrm{THA}_{2}\left[\mathrm{PtCl}_{6}\right]$. By extrapolating the plot to the $y$-axis intercept, a value for the conductivity at infinite dilution, $\Lambda^{0}$ was estimated to be approximately $53.5 \Omega^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$.

The applicability of (5.8) to the experimental data is shown in Figure 5.7. From the extrapolated value for $\Lambda^{0}$, an association constant, $K^{1}$, of approximately $1.1 \times 10^{4}$ was calculated. The large decrease of conductivity with concentration is characteristic of a strongly associated electrolyte. The association constant is related to the distance of closest approach of ions in the ion-pair.

The interatomic distance for $\left[\mathrm{PtCl}_{6}\right]^{2-}$ is $2.316 \AA$ (Table 5.7), ${ }^{308}$ the ionic radius of $\mathrm{Cl}^{-}$ is $1.81 \AA$ (Pauling ${ }^{250}$ ) and the radius of $\mathrm{THA}^{+}$is estimated at $8.56 \AA$ by molecular modelling. From these values, the distance between the centres of the two ions was calculated to be 1.27 nm . The value of $Q$ was found to be 274 and from Bjerrum theory, this corresponds to a distance of closest approach of 1.66 nm , which is in reasonable agreement with the molecular dimensions of the ion-pair, as it is possible that the ions will be solvated and therefore have slightly increased radii.


Figure 5.6 Concentration dependence of the conductivity of $\mathrm{THA}_{2}\left[\mathrm{PtCl}_{6}\right]$ complex


Figure 5.7 Test of equation (5.5)

The value of $\Lambda^{0}$ is approximate, but the purpose of this calculation is only to show that $\left[\mathrm{PtCl}_{6}\right]^{2-}$ must be strongly ion paired and that simple assumptions lead to reasonable ionic dimensions. It can be concluded that the actual values of the transfer potentials will be affected by ionic interactions.

### 5.2 Impedance Spectroscopy of Chloroplatinate Ion Transfer

The study of ion transfer (IT) by the EIS technique has been well reported in the literature. ${ }^{44,46,114,251-253}$ Kakutani et al. ${ }^{254}$ and Sabela et al. ${ }^{116}$ examined the mechanism for ion transfer using AC impedance experiments. Itagaki et al. used the technique to investigate the mechanism of facilitated ion transfer of metallic ions across the water/1,2-DCE interface. ${ }^{251}$

In the present work, EIS measurements have been conducted for the transfers of $\left[\mathrm{PtCl}_{4}\right]^{2-}$ and $\left[\mathrm{PtCl}_{6}\right]^{2-}$ across the water/1,2-DCE interface. The cell used for these measurements was the same as used for electron transfer measurements, described in earlier Chapters, except that large area $\mathrm{Ag} / \mathrm{AgCl}$ electrodes were used in both phases. The cell was of the form:
$\mathrm{Ag} / \mathrm{AgCl} \mid 10 \mathrm{mM}$ THACl $_{(\mathrm{aq})} \mid 10 \mathrm{mM}$ THATPB $_{(1,2-\mathrm{DCE})}$

$$
|\sigma| 50 \mathrm{mM} \mathrm{LiCl}_{(\mathrm{aq})}+0.250 \mathrm{mM}\left[\mathrm{PtCl}_{4 / 6}\right]^{2-} \mid \mathrm{AgCl} / \mathrm{Ag}
$$

The EIS of chloroplatinate ion transfers were some of the last measurements made in this project. Unfortunately, only one data set was obtained for each chloroplatinate as there was insufficient time for repetition of the measurements. Data were treated using method employed for the electron transfer impedance measurements. ${ }^{187,189}$

Figures 5.8 a and 5.8 b show the dependence of $\ln \{\delta /[1+\exp (-b)]\}$ on the reduced potential $b$. The data for ion transfer were visibly noisier than for the ET measurements. This can be attributed in part, to the lower concentration of supporting electrolyte employed in the aqueous phase for the IT measurements, giving rise to a larger cell impedance.

The impedance appeared to increase more quickly on either side of the half-wave potential than was the case for ET measurements. In future measurements more points should be taken closer to the half-wave potential of the platinate ion transfer.

The data for $\left[\mathrm{PtCl}_{4}\right]^{2-}$ can be considered reliable, with eight of the nine measurements falling inside the $95 \%$ confidence interval in Figure 5.8a. ${ }^{255}$ However, the variance $\left(\mathrm{R}^{2}\right)$ of the line of best fit for $\left[\mathrm{PtCl}_{6}\right]^{2-}$ in Figure 5.8 b was below 0.95 , even following the elimination of outliers, therefore this data set must be viewed with some caution.

The calculated values are summarised in Table 5.4. Although the transfer coefficients of the two chloroplatinates were quite different, this was counterbalanced by the difference in the diffusion coefficients for the two ions, which overall resulted in similar values for the rate constants of IT.

Table 5.4 Summary of the results of the EIS of $250 \mu \mathrm{M}\left[\mathrm{PtCl}_{4}\right]^{\mathbf{2 -}}$ and $\left[\mathrm{PtCl}_{6}\right]^{\mathbf{2}}$ ion transfer across the water/1,2-DCE interface.

|  | $\left[\mathrm{PtCl}_{4}\right]^{2-}$ | $\left[\mathrm{PtCl}_{6}\right]^{2-}$ |
| :--- | :---: | :---: |
| Variance, $\mathrm{R}^{2}$ (of Figure 5.8) | 0.967 | 0.939 |
| Diffusion coefficient, $\boldsymbol{D} / \mathrm{cm}^{\mathbf{2}} \mathrm{s}^{-1}$ | $8.9 \times 10^{-6}$ | $4.7 \times 10^{-6}$ |
| Transfer coefficient, $\alpha$ | 0.58 | 0.27 |
| Rate constant, $k / \mathrm{cm} \mathrm{s}^{-1}$ | $6.6 \times 10^{-3}$ | $7.1 \times 10^{-3}$ |



Figure 5.8 Dependence of $\ln \{\delta /[1+\exp (-b)]\}$ on the applied potential for the transfer of (a) $\mathbf{2 5 0}$ $\mu \mathrm{M}\left[\mathrm{PtCl}_{4}\right]^{2-}$ and (b) $250 \mu \mathrm{M}\left[\mathrm{PtCl}_{6}\right]^{2-}$ across the water/1,2-DCE interface.

### 5.3 Effect of Aqueous Ligand on Chloroaurate Transfer

In the previous sections it has been shown that the transfer potential can be altered by ion-pairing in the organic phase. The control of the transfer potential is a central issue in metal ion separations and for this reason a ligand for gold in the aqueous phase was investigated. The control of the Au (III) transfer was also important for being able to use ketones as solvents for metal ion separations; it will be shown in a later chapter that ketones can act as reducing agents for $\left[\mathrm{AuCl}_{4}\right]^{\circ}$. Therefore a complexing agent that would bind to $\mathrm{Au}(\mathrm{III})$ and a) prevent its transfer to the organic phase and b) prevent its reduction by ketones, was investigated. It has been suggested ${ }^{256}$ that a tetraalkylphosphonium salt such as tetrakishydroxymethylphosphonium chloride $\left(\mathrm{HOCH}_{2}\right)_{4} \mathrm{PCl}$, might be useful for this purpose, due to its ability to coordinate to chloroaurate anions ${ }^{257}$ and allow an improvement in the separation of platinum and gold. In the following experiments, the potentials refer to the cell:
$\mathrm{Ag} / \mathrm{AgCl}\left|10 \mathrm{mM} \operatorname{TPAsCl}_{(\mathrm{aq})}\right| 1.5 \mathrm{mM} \operatorname{TPAsTPB}_{(\mathrm{o})}|\sigma| 10 \mathrm{mM} \mathrm{LiCl}_{(\mathrm{aq})} \mid \mathrm{AgCl} / \mathrm{Ag}$

The organic phase consisted of $70 \% 1,2-\mathrm{DCE}$ and $30 \% 1,3$-difluorobenzene. The transfer of $\mathrm{Pt}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{IV})$ (both $100 \mu \mathrm{M}$ ) was compared with that of $\mathrm{Au}(\mathrm{III})$ (146 $\mu \mathrm{M}$ ) both in the absence and presence of the aqueous ligand. Figure 5.9a shows that the transfer of the three species can be observed. However, on addition of tetrakishydroxymethylphosphonium chloride $(0.4 \mathrm{mM})$, the peak corresponding to the transfer of $\mathrm{AuCl}_{4}{ }^{-}$to the organic phase disappeared but the Pt peaks remained unaffected (Fig. 5.9b).


Figure 5.9 a) faint line $=$ baseline, bold line $=$ following the addition of $\left(100 \mu \mathrm{M}\left[\mathrm{PtCl}_{4}\right]^{\mathbf{2 -}}, 100 \mu \mathrm{M}\right.$ $\left[\mathrm{PtCl}_{6}\right]^{2-}$ and $\left.146 \mu \mathrm{M} \mathrm{AuCl}_{4}\right)$.
b) faint = as for bold line in (a), bold = following the addition of $0.4 \mathbf{~ m M}$ hydroxymethylphosphonium chloride.
c) faint $=$ as for bold line in (b), bold= following the addition of $0.8 \mathrm{mM}\left[\mathrm{AuCl}_{4}\right]^{-}$.

If an excess of chloroaurate ( 0.8 mM ) was added to the solution in concentrations greater than that of the ligand, the gold transfer was again observed (Fig. 5.9c), indicating that the complexation by the phosphonium salt is very strong and shifts the transfer potential of Au (III) outside the potential window.

### 5.4 Solvent Effects

The influence of the solvent on the difference of Galvani transfer potential between $\left[\mathrm{PtCl}_{4}\right]^{2-}$ and $\left[\mathrm{PtCl}_{6}\right]^{2-}$ was studied. This was important in order to optimise separations and investigate the influence of the solvent for distinguishing between planar and octahedral complexes. This difference is referred to as $\delta \Delta_{0}^{\omega} \phi$ and the results obtained are summarised in Table 5.5.

Simple ion transfers of $\left[\mathrm{PtCl}_{4}\right]^{2-}$ and $\left[\mathrm{PtCl}_{6}\right]^{2-}$ (Fig. 5.10a and b) from aqueous solution to MIBK were observed. The use of MIBK as a solvent for electrochemical studies is relatively novel and the standard potential of the transfer from water to MIBK for the $\mathrm{THA}^{+}$ion is not available. The potentials reported are therefore applied potentials and are not given on the Galvani scale. The difference between the half-wave transfer potentials for $\left[\mathrm{PtCl}_{4}\right]^{2-}$ and $\left[\mathrm{PtCl}_{6}\right]^{2-}$ from water to MIBK was 50 mV .

The transfer of $\left[\mathrm{AuCl}_{4}\right]^{-}$and $\left[\mathrm{PdCl}_{4}\right]^{2-}$ was also investigated. Cheng et al. ${ }^{244}$ observed the simple ion transfer of $\left[\mathrm{AuCl}_{4}\right]^{-}$from water to $1,2-$ DCE. However, when MIBK was used as the organic solvent, the $\left[\mathrm{AuCl}_{4}\right]^{-}$transfer was no longer reversible and the voltammetry quickly degraded due to the formation of a metal film at the water/MIBK interface, which will be discussed in Chapter 7.

Cheng et al. ${ }^{244}$ observed the facilitated ion transfer of $\left[\mathrm{PdCl}_{4}\right]^{2-}$ from water to $1,2-$ DCE in the presence of dibutylthiourea (DBTU).

Simple ion transfer of $\left[\mathrm{PdCl}_{4}\right]^{2-}$ from water to MIBK was not observed electrochemically, in agreement with the results for 1;2-DCE. However, when using DBTU as the ligand in MIBK, $\left[\mathrm{PdCl}_{4}\right]^{2-}$ transfer was still not observed. It is proposed that $\left[\mathrm{PdCl}_{4}\right]^{2-}$ transfers into MIBK outside the available potential window. The transfer also occurred in the absence of applied potential; this was visible as the yellow palladium complex transferred from the aqueous to the organic phase. The complex also appeared to be reduced by the solvent, giving a grey suspension in the aqueous solution. However, the rate of reduction of the palladates was much slower than that of chloroaurate.

Table 5.5 Difference in Galvani potential of ion transfer, $\delta \Delta_{o}^{w} \phi$, between $\left[\mathrm{PtCl}_{4}\right]^{2-}$ and $\left[\mathrm{PtCl}_{6}\right]^{2-}$ for different solvents.

| Water / Solvent | Relative Permittivity ( $\varepsilon)$ | $\delta \Delta_{o}^{\omega} \phi\left[\mathrm{PtCl}_{4 / 6}\right]^{2-}$ |
| :--- | :---: | :---: |
| 1,2-DCE | 10.42 | 110 mV |
| $70 \%$ 1,2DCE / 30\% m-DFB | $10.42 / 5.02$ | 95 mV |
| MIBK | 13.1 | 50 mV |
| 2-Octanone | 9.51 | 40 mV |



Figure 5.10 Transfer of (a) $\left[\mathrm{PtCl}_{4}\right]^{2-}$ and (b) $\left[\mathrm{PtCl}_{6}\right]^{2-}$ across the water/MIBK interface for different concentrations, sweep rate $=10 \mathrm{mV} \mathrm{s}^{-1}$.

### 5.5 Redox Switchable Ligand

Besides using transition metal ligands, electrochemical measurements have been conducted on the commercially available redox switchable ligand $\mathrm{N}, \mathrm{N}$ dimethylaminomethylferrocene (DMAMF). The use of tertiary amines ${ }^{258}$ or quaternary ammonium salts is well known in metal ion extraction. ${ }^{166,167}$ The nitrogen in DMAMF should be able to coordinate to transition metal cations and therefore, it was expected that the bond strength should be dependent on the electron density in the ferrocene moiety. Thus, it was interesting to explore the possibility of alternating coordination by a redox process. Preliminary experiments were carried out with copper (II) complexes with the above ligand.

Figure 5.11 shows the voltammetric response of a 1 mM concentration of DMAMF in an aqueous solution of $\mathrm{LiCl}(10 \mathrm{mM})$ at a gold electrode (thin line). DMAMF gave a single redox wave with $E_{1 / 2}=0.20 \mathrm{~V}$, corresponding to the following redox reaction:

$$
\begin{equation*}
\mathrm{DMAMF} \leftrightarrows \mathrm{DMAMF}^{+}+\mathrm{e}^{-} \tag{5.9}
\end{equation*}
$$

The presence of a 0.2 mM concentration of $\mathrm{Cu}\left(\mathrm{ClO}_{4}\right)_{2}$ (heavy line) caused a slight decrease in the peak current of the wave at $E_{1 / 2}=0.2 \mathrm{~V}$, also a second wave with $\mathrm{E}_{1 / 2}$ $=0.375 \mathrm{~V}$ could be seen. The formation of heterobimetallic organo metal chelates of DMAMF with selected main group and transition metal has been discussed by Jacob et al. ${ }^{259}$. It is therefore proposed that the nitrogen in the amino- group of DMAMF will be able to coordinate to the copper ions in solution. The coordination of the copper will withdraw electron density from the cyclopentadiene rings of the
ferrocene, making the oxidation of ferrocene to ferrocenium more difficult. This corresponds to a shift to a higher potential for the redox wave of DMAMF. The possibility that the $\mathrm{Cu}(\mathrm{II})$ is deposited on the Au electrode has also been considered and discounted. ${ }^{260}$

Figure 5.12 shows the result of a liquid/liquid experiment using the cell:

$$
\begin{aligned}
& \mathrm{Ag} / \mathrm{AgCl}\left|10 \mathrm{mM} \mathrm{TPAsCl}_{(\mathrm{aq})}\right| 10 \mathrm{mM} \operatorname{TPAsTPB}_{(0)}|\sigma| \\
& 10 \mathrm{mM} \mathrm{LiCl}_{(\mathrm{aq})}+0.141 \mathrm{mM} \text { DMAMF }+\mathrm{x} \mathrm{mM} \mathrm{CuCl} 2 \mid \mathrm{AgCl} / \mathrm{Ag}
\end{aligned}
$$

$\mathrm{CuCl}_{2}$ was used in the place of $\mathrm{Cu}\left(\mathrm{ClO}_{4}\right)_{2}$ as the ion transfer of the $\mathrm{ClO}_{4}{ }^{-}$would have been seen inside the potential window. In the absence of $\mathrm{CuCl}_{2}$ (faintest line) a wave with $\Delta_{o}^{w} \phi=0.20 \mathrm{~V}$ was observed. No redox couple was present in the organic phase, therefore the wave cannot correspond to an electron transfer reaction, and must therefore be due to the transfer of DMAMF or of a charged complex of DMAMF from the aqueous to the organic phase.

This was unexpected as the Fe centre of the ferrocene moiety in DMAMF should be in the +2 oxidation state, therefore the complex would carry no overall charge and the transfer would not be measurable voltammetrically. It is possible that the aminogroup of DMAMF is either:-(i) protonated in the aqueous phase or (ii) forms an interfacial ion pair with the organic supporting electrolyte cation. The transfer observed would correspond to the facilitated ion transfer of DMAMF. ${ }^{261}$

In the presence of $\mathrm{CuCl}_{2}$, a second wave could be seen at $\Delta_{o}^{w} \phi=0.02 \mathrm{~V}$ this was accompanied by a corresponding decrease in the intensity of the wave at $\Delta_{o}^{w} \phi=0.20$ V. The second wave should correspond to the transfer of DMAMF, as $\mathrm{Cu}(\mathrm{II})$ transfer is known to occur outside of the potential window. ${ }^{63}$ The change in the transfer potential of DMAMF could be attributed to a change in the electron density of DMAMF upon complexation with $\mathrm{Cu}(\mathrm{II})$, however it is noted that steric hinderance of the tertiary amine group by the methyls may prevent this effect. It is also possible that the change in transfer potential is due to a change in pH of the aqueous phase upon addition of the Cu (II).

When $175 \mu \dot{\mathrm{M}} \mathrm{Cu}(\mathrm{II})$ had been added, the wave at $\Delta_{0}^{w} \phi=0.20 \mathrm{~V}$ had completely diminished. Figure 5.13 shows that the DMAMF/Cu(II) complex gave a reversible transfer with a peak separation of approximately 70 mV , close to the value expected for the transfer of a singly charged species (1.12). A plot of the square root of the sweep rate versus peak current density gave a linear plot (Fig. 5.14), from which a diffusion coefficient, $\mathrm{D}=1.58 \times 10^{-5} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$ was calculated.

Increasing the concentration of DMAMF resulted in an increase in the peak current of the wave at $\Delta_{o}^{w} \phi=0.02 \mathrm{~V}$, corresponding to uptake of the previous excess of $\mathrm{Cu}(\mathrm{II}),(\mathrm{Cu}(\mathrm{II}): \mathrm{DMAMF}=175: 141)$. The addition of DMAMF to excess caused the wave at $\Delta_{o}^{w} \phi=0.20 \mathrm{~V}$ to return. With current responses directly proportional to the ratio of DMAMF: $\mathrm{Cu}(\mathrm{II})$, it is concluded that $\Delta G_{\text {trans }}$ of DMAMF is decreased by the addition of $\mathrm{Cu}(\mathrm{II})$ to the aqueous phase. The effect of DMAMF is that it brings the
transfer of copper into the potential window, ${ }^{151}$ therefore DMAMF can be considered as a promising candidate for the facilitated ion transfer of $\mathrm{Cu}(\mathrm{II})$.


Figure 5.11 Cyclic voltammogram of 1 mM DMAMF in the absence (faint line) and presence (heavy line) of $0.2 \mathrm{mM} \mathrm{Cu}\left(\mathrm{ClO}_{4}\right)_{2}$. Sweep rate $=50 \mathrm{mV} \mathrm{s}^{-1}$.


Figure 5.12 Cyclic voltammogram of 0.141 mM DMAMF in the absence of $\mathrm{CuCl}_{2}$ (faintest line) and the presence (heavier lines) of increasing concentrations of $\mathrm{CuCl}_{2}$. Sweep rate $=50 \mathrm{mV} \mathrm{s}{ }^{-1}$.


Figure 5.13 Cyclic voltammogram of 0.141 mM DMAMF/Cu(II) complex ion transfer across the water/1,2-DCE interface with increasing sweep rate.


Figure 5.14 Dependence of peak current density on sweep rate for the transfer of the DMAMF/Cu(II) complex across the water/1,2-DCE interface.

### 5.6 Ionic Solvation and Molecular Modelling

The Gibbs energy of transfer, and so the galvani potential of ion transfer of the platinates will depend strongly on short range ion-solvent interactions. Factors contributing to these solvent-ion interactions include:

- The oxidation state of the platinum ion centre. This governs the geometry of the complex, see Figure 5.15. Square planar $\mathrm{Pt}(\mathrm{II})$ complexes have more negative transfer potentials than the equivalent octahedral $\mathrm{Pt}(\mathrm{IV}$ ) complex (see Table 5.3).
- The electronegativity of the coordinated ligands, which determines the distribution of electron density over the surface of the complex. Molecular modelling has been used to yield this information for the anti-tumor compound cisplatin [cis-diamminedichloroplatinum(II)] and the analogue carboplatin. ${ }^{262,263}$
- The dielectric permittivity and coordinating ability of the organic solvent.


### 5.6.1 Ion-Solvent Interaction

Born discussed the interaction between ion and solvent, ${ }^{264}$ describing the changes in the standard molar individual thermodynamic functions for the transfer of an ion from the gas phase into a solvated state, in terms of the relative permittivities of the two environments. The electrostatic work performed in discharging the ion, solvating the ion in a solvent of dielectric permittivity $\varepsilon_{0}$, then recharging the ion was given by the Born equation:

$$
\begin{equation*}
\Delta G_{s}^{\theta}=\frac{-z^{2} e^{2} N_{A}}{8 \pi \varepsilon_{0} r_{i}}\left(1-\frac{1}{\varepsilon_{r}}\right) \tag{5.10}
\end{equation*}
$$



Figure 5.15 Comparison of crystal field splitting diagrams for octahedral $\operatorname{Pt}(\mathrm{IV})$ and square planar Pt(II)
where $z$ and $r_{i}$ are the charge number and the radius of the ion respectively. $N_{A}$ is Avagadro's number and $\varepsilon_{0}$ is the vacuum permittivity.

Abraham and Liszi described the energetics of solvation of an ion. ${ }^{265}$ They listed the required energy terms as:

- The energy required for formation of an appropriately sized cavity in the solvent.
- The energy required to move the solvent molecules into the appropriate layers.
- The electrostatic energy of interaction of the ion with the solvent in the layers and with the bulk solvent beyond.
- The non-electrostatic energy of interaction of the ion with near neighbour solvent molecules.
- A correction term for different standard states.

They noted that calculations based on the individual terms would be difficult, however, if the ion were replaced by a non-polar solute of the same radius as the ion the only term outstanding would be the electrostatic term. If this term were denoted by $\Delta G_{e}^{0}$, then:
$\Delta G_{\mathrm{s}}^{0}=\Delta G_{\mathrm{e}}^{0}+\Delta G_{\mathrm{n}}^{0}$

Where the subscripts s, e and n indicate the solvation, electrostatic and non-polar terms respectively. They proposed a continuum model in which an ion of radius $a$ and relative permittivity $\varepsilon_{\mathrm{i}}$ is surrounded by a local solvent layer of thickness $(b-a)$ of
dielectric permittivity $\varepsilon_{1}$, immersed in the solvent of bulk dielectric permittivity $\varepsilon_{0}$. The structure of this model was in many ways similar to a qualitative model proposed earlier by Frank and Wen. ${ }^{266}$ Abraham and Liszi's model was later extended to cover two solvent layers, ${ }^{267}$ and to the investigation of entropies of solvation. ${ }^{268,269}$

Marcus reviewed the structural aspects of ionic solvation. ${ }^{270}$ An ion with a net negative charge across the surface will be solvated with the protons of the water dipoles in the inner solvation shell oriented towards the ion. ${ }^{245,271}$ The classical structural approach to the hydration of small ions and the structure of $\mathrm{H}_{2} \mathrm{O}$ was made in the 1930's by Bernal and Fowler. ${ }^{272}$ They proposed that water would orient about an ion as shown in Figure 5.16, where $\rightarrow+$ represents the water molecule dipole.



Figure 5.16 Bernal and Fowler model for the orientation of water molecules with respect to positive and negative ions.

A discussion of the thermodynamics of their model is not necessary here, as the Bernal and Fowler model for anionic solvation was later discarded ${ }^{271}$ in favour of that proposed by Buckingham. ${ }^{273}$ Buckingham highlighted that in the earlier models it had been assumed that the most favourable orientation of a water molecule next to a negative ion, was one in which a protons was placed on a line joining the centre of the ion to the oxygen atom. He noted that this required the dipole of the water to lie
at an angle of $52^{\circ}$ to the electric lines of force. He suggested that a minimum dipolar interaction energy could be obtained with an angle of $0^{\circ}$, a representation of this orientation is given in Figure 5.17 below.


Figure 5.17 Buckingham model for the orientation of water molecules with respect to an anion.

Subsequent studies have shown that for anions neither model is correct, as there are major entropic considerations. The ionic hydrogen-bonds act to disrupt or reinforce networks of water molecules around the solvated ion, this depends strongly upon the ion being solvated. Fluoride is considered to reinforce such networks and is considered a "structure maker" whilst iodide is considered to hinder the formation of water networks and is described as a structure breaker. ${ }^{270}$ In a recent spectroscopic study, Ayotte et al. ${ }^{274}$ examined the interplay between ion-water and water-water interactions in halide ion - water clusters. Their results for $\mathrm{X}^{-} .\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$ suggest that the Bernal and Fowler model is perhaps more close to the true case than the Buckingham model which would preclude the formation of ionic hydrogen-bonding interactions between neighbouring water molecules on the same ionic centre.

Which ever model is adopted, it is clear that moving from the solvation of a spherical monoatomic anion such as the halides to a non-spherical polyatomic anion e.g. a platinate will make it harder still to understand the way in which the ion is solvated.

Osakai et al. ${ }^{107,108}$ studied the ion transfer of several large oxygen containing polyanions including $\left[\mathrm{VMo}_{5} \mathrm{O}_{19}\right]^{3-},\left[\mathrm{Mo}_{8} \mathrm{O}_{26}\right]^{4-},\left[\mathrm{Mo}_{6} \mathrm{O}_{19}\right]^{2-}$ and $\left[\mathrm{SiMo}_{12} \mathrm{O}_{40}\right]^{4-}$. They assumed that a polyanion containing a given number of oxygens was a hard sphere of uniform surface charge and that there was a direct relationship between the calculated surface charge density and the Galvani potential of ion transfer. There was, however, no linear relationship between the surface charge density and the standard Gibbs energy of transfer.

### 5.6.2 Molecular Modelling of Platinates

Molecular modelling is a constantly expanding field, ${ }^{275,276}$ to a large extent due to the great advances in computer technology, which over the last decade have seen the cost of workstations fall by an order of magnitude. ${ }^{277}$ The application of molecular modelling techniques to the transfer of ions across the liquid/liquid interface could - $-\cdots$ offer an insight into the details of the charge transfer process. There have been several publications utilising molecular dynamics to model the structure of the interface. These were mentioned briefly in the Introduction, but with the exception of the work of Osakai et al. ${ }^{107,108,278}$ few studies appear to have been carried on the nature of the ions which undergo transfer through the interface and their interaction with the solvent. This section describes the modelling of the platinate ions since considerable information has been obtained in this work on the dependence of transfer potentials on the ligands surrounding the metal ions.

By modelling the charge, due to the geometry and electronegativity of polyatomic anion ligands, e.g. for a hexahaloplatinate, an understanding of the interaction of the ion by water molecules might be gained.

### 5.6.2.1 Quantum Mechanical Methods

Quantum mechanical methods deal with the electrons in a system, even if some of them are ignored (semi-empirical methods). The calculations required are relatively large and time consuming, which leads to long computation times when using desktop molecular modelling (DTMM) packages such as HyperChem. ${ }^{279}$ Most of the commercially available DTMM packages have been written to satisfy the modelling requirements of organic chemists and until recently few of the semi-empirical methods available contained the parameters required for modelling metal complexes.

Several computational studies are closely related to the present work, ${ }^{262,263}$ in which calculations were made using density functional theory (DFT), an alternative to $a b$ initio calculations. DFT stems from work in 1964 by Hohenberg and Kohn ${ }^{280}$ and popularised by Car and Parrinello ${ }^{281}$ in the 1980 s. The theory was built on the electron density of the atoms in a molecule and the aim is to design functionals ${ }^{282}$ connecting the electron density of a molecule or ion to its energy.

### 5.6.2.2 Molecular Mechanics

Molecular Mechanics (MM) ${ }^{283}$ is an empirical method traditionally employed for modelling systems too large to be tackled with quantum mechanical methods. It has been used primarily for conformational analysis. There are many MM force fields available. Unfortunately, few of the force fields which have been developed contain parameterisation for heavier elements ${ }^{284}$ and those which have tend not to cover the third row of the transition elements where it is important to address relativistic effects. Exceptions include the Universal Force Field (UFF), so called because, unlike many MM force fields, it was claimed to be parameterised for almost the
whole periodic table, including platinum, ${ }^{285-287}$ and the SHAPES force field, parameterised specifically for square planar coordination complexes. ${ }^{288}$

MM has been used for the modelling of coordination compounds ${ }^{289}$ and some investigations for $\mathrm{Pt}(\mathrm{II})$ complexes have been presented. ${ }^{290}$ Even though account is often taken of the electronic properties of the metal ion centre, the overall aim in most of these studies are to find: (i) which conformations are stable; (ii) which are the preferred conformations and (iii) energy differences between stable conformations. A good example was provided by Yao et al. who used an AMBERtype force field to examine the interaction of $\mathrm{Pt}(\mathrm{II})$ amines with guanine. ${ }^{291}$ MOMEC97 is a molecular mechanics system developed primarily for strain energy minimisation of metal complexes. ${ }^{292,293}$ In the present work it was not possible to use this package to provide realistic values for the charge on each of the atoms of a simple platinum complex such as $\left[\mathrm{PtCl}_{4}\right]^{2-}{ }^{294}$

A limitation of MM calculations is that they usually refer to molecules in vacuum, and only recently it has become possible to incorporate the solvent in the calculations. For instance, Rasaiah calculated the solvent structure around some metal cations and halides at infinite dilution using molecular dynamics simulations. ${ }^{295}$ The mobility of the ion was suggested to be strongly influenced by the orientation of the water molecules in the primary solvation shell. For $\mathrm{Li}^{+}$it was calculated that four water molecules were oriented approximately tetrahedrally around the ion, with the oxygen atoms pointing inwards. In the case of $\mathrm{F}^{*}$ the primary hydration shell consists of approximately 6-7 water molecules with the protons pointing towards the ion. This is in reasonable agreement with the results
from Monte Carlo simulations performed by Chandrashekhar et al. ${ }^{296}$ in the early 1980s, where the numbers of water coordinating to $\mathrm{Li}^{+}, \mathrm{Na}^{+}, \mathrm{F}^{-}$and $\mathrm{Cl}^{-}$were $5,6,6$ and 7 respectively.

The most relevant examples for the present work include the $a b$ initio calculations by Lin and Hall ${ }^{297}$ who studied the mechanism of substitution reactions for squareplanar transition metal complexes. Effective core potentials were used and geometries optimised using a restricted Hartree-Fock basis set. Work by Panina and Kukushkin ${ }^{298,299}$ was done using semi empirical CNDO and $a b$ initio Hartree-FockRoothan method with the Gaussian-92 program was used to examine the coordination complexes of amidine and acetonitrile with $\mathrm{Pt}(\mathrm{II})$ and $\mathrm{Pt}(\mathrm{IV})$. Molecular orbitals energies were calculated in order to predict the reactivity of the organic ligand in the coordinated and uncoordinated state. Recently, Pavankumar et al. ${ }^{300}$ Chval and $\mathrm{Sip}^{301}$ and Kozelka et al. ${ }^{302,303}$ carried out ab initio calculations to model the interaction between the platinum atom in cisplatin and sequences of DNA.

### 5.6.2.3 Density Functional Theory (DFT)

Unfortunately, whilst being relevant, most of the above studies were too specific to be applied to the present work. Carloni et al. ${ }^{262,263}$ used density functional theory to investigate the electronic and structural properties of cisplatin, their work was based around the successive substitution of the chlorides on $a \cdot\left[\mathrm{PtCl}_{4}\right]^{2-}$ centre by ammonia molecules. As mentioned previously, tetrachloroplatinate was one of the main ions studied in the present work. In a separate work, Deeth employed DFT to study the bond lengths in $\left[\mathrm{MX}_{6}\right]^{2-}$ molecules including hexabromo- and hexachloroplatinates. ${ }^{304}$ The interest in relation to the present work is that DFT
calculations could yield values for isodensity surfaces of the electron density or electronic distribution over the surface of highly symmetrical $\left(\mathrm{D}_{4 \mathrm{~h}}, \mathrm{O}_{\mathrm{h}}\right)$ platinum anions. Such data would be useful for comparison with the Galvani potential of ion transfer.
$\mathrm{Pt}(\mathrm{II})$ and the corresponding $\mathrm{Pt}(\mathrm{IV})$ ions will have different electronic configurations. Figure 5.15 showed a simple crystal field splitting diagram ${ }^{305}$ for the two ions. It is reasonable to assume that their complexes will have different electron densities over the surface of the ion. The cartoons in Figure 5.18 show the space filled representations of: a) $\left[\mathrm{Pt}(\mathrm{CN})_{4}\right]^{2-}$ b) $\left[\mathrm{Pt}(\mathrm{CN})_{6}\right]^{2-}$ c) $\left[\mathrm{PtCl}_{4}\right]^{2-}$ and d) $\left[\mathrm{PtCl}_{6}\right]^{2-}$ as calculated by the CAChe molecular modelling package ${ }^{306}$ on a Macintosh P.C.

The square planar Pt (II) complexes have a net charge of -2 distributed between four ligands which are equatorial to the platinum ion centre. In a hypothetical case, if the overall charge on the $\mathrm{Pt}(\mathrm{II})$ centre were zero, then each of the ligands would carry a charge of -0.5 . From simple consideration of charge distribution, and from the vacancy of the $5 \mathrm{~d}_{z^{2}}$ orbital, the negative charge must be concentrated equatorially about the ion as can be seen in Figure 5.18a, thus the axial positions should carry a less negative charge than the equatorial positions.

For an equivalent octahedral $\mathrm{Pt}(\mathrm{IV})$ complex, if the platinum ion centre were to carry no overall charge, the -2 charge of the ion would be distributed between six ligands and each of the ligands would carry an overall charge of -0.33 . Figure 5.18 b shows that this negative charge would be distributed more evenly around the platinum ion centre, making both axial and equatorial positions equally negative.

c) representation of $\left[\mathrm{PtCl}_{4}\right]^{2-}$
b) representation of $\left[\mathrm{Pt}(\mathrm{CN})_{6}\right]^{2-}$

d) representation of $\left[\mathrm{PtCl}_{6}\right]^{2-}$

The way in which the solvent coordinates to the ion will be dependent on the surface charge that it sees at different locations around the ion.

The values for the charge distribution about platinum anions could not be obtained from HyperChem (Hypercube Inc.), CAChe (Oxford Molecular) or MOMEC97 (University of Heidelberg). Fortunately, an expert in DFT was willing to perform preliminary calculations. Deeth ${ }^{307}$ has made calculations for the tetra- and hexa-chloro-, bromo- and cyanoplatinates and produced Mulliken point charges for the platinum centre and the atoms of the ligands.

### 5.6.3 DFT Results

The DFT calculated interatomic distances are shown in Table 5.6. These compare well with the values obtained from crystallographic data given in Table 5.7. ${ }^{308}$ The dependence of the Galvani potential of ion transfer on the point charge on the ligand (Figure 5.18) shows a good correlation, in agreement with the results of Osakai et al. where the surface charge density was found to give a similar relationship. ${ }^{108,278}$ Further refinements of this DFT approach would require the inclusion of a dielectric continuum in the model and to monitor the polarisability of the ions in response to placing the ion in solvents of different dielectric permittivity. Another approach would be to use the DFT output of the polarised complexes in conjunction with a package such as HyperChem, defining and freezing the point charges on atoms, then placing the ion in a periodic box and calculating how a small number of water molecules orient around the ion. This was beyond the scope of the present work.

Table 5.6 DFT Calculated bond lengths.

| Complex | $\mathbf{P t - L} / \AA$ | $\mathbf{C - N} / \AA$ |
| :---: | :---: | :---: |
| $\left[\mathrm{PtCl}_{4}\right]^{2-}$ | 2.311 | - |
| $\left[\mathrm{PtBr}_{4}\right]^{2-}$ | $\mathrm{Br}[3 \mathrm{~d}]: 2.471$ |  |
| $\mathrm{Br}[3 \mathrm{p}]: 2.453$ | - |  |
| $\left[{\left.\mathrm{Pt}(\mathrm{CN})_{4}\right]^{2-}}^{\left[\mathrm{PtCl}_{6}\right]^{2-}}\right.$ | 1.978 | 1.170 |
| $\left[\mathrm{PtBr}_{6}\right]^{2-}$ | 2.314 | - |
| $\left[{\left.\mathrm{Pt}(\mathrm{CN})_{6}\right]^{2-}}^{\operatorname{Br}[3 \mathrm{~d}]: 2.507} \begin{array}{c}\mathrm{Br}[3 \mathrm{p}]: 2.483 \\ 1.960\end{array}\right.$ | - |  |

Table 5.7 Interatomic distances obtained from the Cambridge Structural Database. ${ }^{308}$

| Complex | No. of examples | $\mathbf{P t - L} / \AA$ | $\mathbf{C - N} / \AA$ |
| :---: | :---: | :---: | :---: |
| $\left[\mathrm{PtCl}_{4}\right]^{2-}$ | 39 | $2.301 \pm 0.007$ | - |
| $\left[\mathrm{PtBr}_{4}\right]^{2-}$ | 3 | $2.409 \pm 0.011$ | - |
| $\left[{\left.\mathrm{Pt}(\mathrm{CN})_{4}\right]^{2-}}^{\left[\mathrm{PtCl}_{6}\right]^{2-}}\right.$ | 23 | $1.983 \pm 0.015$ | $1.149 \pm 0.018$ |
| $\left[\mathrm{PtBr}_{6}\right]^{2-}$ | 41 | $2.316 \pm 0.007$ | - |
| $\left[{\left.\mathrm{Pt}(\mathrm{CN})_{6}\right]^{2-}}^{2}\right.$ | $2.460 \pm 0.004$ | - |  |

Table 5.8 DFT calculated Mulliken Atomic Charges.

| Complex | Metal | Ligand | Nitrogen of CN |
| :---: | :---: | :---: | :---: |
| $\left[\mathrm{PtCl}_{4}\right]^{2-}$ | 0.28 | -0.57 | - |
| $\left[\mathrm{PtBr}_{4}\right]^{2-}$ | 0.45 | -0.61 | - |
| $\left[{\left.\mathrm{Pt}(\mathrm{CN})_{4}\right]^{2-}}^{\left[\mathrm{PtCl}_{6}\right]^{2-}}\right.$ | 0.15 | -0.14 | -0.40 |
| $\left[\mathrm{PtBr}_{6}\right]^{2-}$ | 0.33 | -0.39 | - |
| $\left[\mathrm{Pt}^{2-} \mathrm{CN}_{6}\right]^{2-}$ | 0.41 | -0.40 | - |



Figure 5.19 Dependence of the Galvani potential on the charge on the ligand.

## 6 Supported Liquid Membranes

Since the early days of liquid/liquid electrochemistry studies, it was hoped to use this technique as an idealised system to model charge transport occurring across interfaces in biological systems ${ }^{309}$; "Ion transport across a membrane is an ubiquitous phenomenon in biological systems as well as other artificial membrane systems for selective detection and separation of ions". ${ }^{310}$ In order to improve the mimetic quality of the model, the interface can be modified in several ways. Perhaps of more immediate interest is the possibility of utilising these interfaces for specific metal ion-separations since ion transfer can be controlled by both the applied potential and the ligands employed. Although these factors are now reasonably well understood, little work has been carried out for the development of practical separation systems.

In this Chapter, a brief overview of types of membrane supported liquid/liquid interfaces as well as methods of study of practical separation modules will be given. The electrochemical characterisation of an SLM extraction system for the separation of $\left[\mathrm{PtCl}_{6}\right]^{2-}$ and $\mathrm{Cu}^{2+}$, some preliminary results and the difficulties encountered will be presented.

### 6.1 The Supported Liquid/Liquid Interface

### 6.1.1 Bilayer Lipid Membranes

Much work has been carried out examining bilayer lipid membranes (BLM), or halfbilayers e.g. monolayers of lipids. ${ }^{311}$ Kakiuchi compared the properties of the BLM
and the liquid/liquid interface. ${ }^{310}$ Kihara et al. also provided a useful review comparing BLMs with liquid membranes. ${ }^{312}$

### 6.1.2 Micro-holes

Girault et al. used thin polyester films with a single micro-hole of well defined geometry, accurately drilled in the film using an excimer laser. ${ }^{313,314}$ Quinn et al. used microholes to study electron transfer reactions across the water/o-NPOE interface. ${ }^{134}$ These techniques can present unusual complications, for example Wilke and Zerihun examined diffusional properties of microholes and found that the thickness of the polymer film and the hole radius influenced the standard potential of ion transfer. ${ }^{315}$ Recent work by Dryfe and Krajl has used track-etched polyester membranes with pore radii of 100 and 15 nm to study ion transfer. ${ }^{316}$ These etched membranes might be considered as an "half-way house" between the laser drilled . $-=$ micro-holes and porous membranes which have a less well defined pore geometry.

### 6.1.3 Porous Membranes

Separation of the two phases by a porous membrane is another method for stabilising the interface, forming a supported liquid membrane (SLM). In addition to electrochemical methods, there are numerous non-electrochemical studies which have utilised SLMs for the selective extraction of target ions, which makes them of great interest for the present work.

A few examples of work to date include that of Ohki et al. ${ }^{317}$ who utilised a Duraguard polypropylene film of thickness $25 \mu \mathrm{~m}$ to support a diphenyl ether
organic phase containing bathocuprine for the selective extraction of Cu (II). Huang and Huang ${ }^{318}$ used a Millipore Durapore polyvinylidene fluoride (PVDF) membrane, thickness $125 \mu \mathrm{~m}$, to support a water/kerosene interface, for the tributyl phosphate assisted extraction of uranyl nitrate. Huang ${ }^{319}$ again used a PVDF membrane for the transport of copper, cobalt, nickel and zinc transport across a kerosene SLM, this time using di(2-ethylhexyl) phosphoric acid (D2EHPA) to facilitate the transfer. Shinbo et al. ${ }^{320}$ made a study of the effect of the solvent on the transport efficiency in an amino acid enantioselective Duraguard poly(propylene) membrane. The selectivity was induced by the use of crown ethers. The membrane solvents used were generally less volatile than $1,2-$ DCE and it was concluded that amongst the solvents tested, o-NPOE and p-nitrophenyl heptyl ether ( $p-\mathrm{NPHE}$ ) were the best, showing long term stability as well as a high transport efficiency. Parthasarathy and Buffle ${ }^{321}$ used a Cellguard 2500 polypropylene hydrophobic membrane treated with a lipophilic crown ether 1,10-didecyl-1,10-diaza-18-crown-6 (commercially available as Kryptofix 22DD) for the separation of transition metal ions, especially Cu (II). The organic phase was a $3: 1$ toluene-kerosene mixture. Kerosene was present only to lower the rate of evaporation from the membrane surface in contact with air. Hundhammer et al. ${ }^{322}$ followed anion transfer across the water/nitrobenzene interface stabilised by a hydrophilic cellulose membrane; the transfer was observed to be reversible at low sweep rates. In later work, Hundhammer et al. ${ }^{323}$ used a hydrophilic dialysis membrane, thickness $\sim 40 \mu \mathrm{~m}$, to support a water/nitrobenzene interface; facilitated transfer of some monovalent cations for use in clinical applications such as the analysis of blood serum were reported.

Katsu et al. ${ }^{324}$ used a methyl ammonium selective membrane produced by casting an amine ionophore with bis(2-ethylhexyl)sebacate as the membrane solvent in a polyvinyl chloride matrix. Wilke and Picht ${ }^{355,326}$ considered the diffusion of thiocyanate, iodide and dodecyl sulfate across a water/nitrobenzene interface supported by an hydrophilic cellulose filter membrane. It was noted that the diffusion coefficient of the singly charge anions under consideration was between one half and one third of its value in water, but it was still higher than the diffusion coefficients observed for dialysis membranes. Wilke et al. ${ }^{327}$ also used a hydrophilic cellulose dialysis membrane to stabilise the interface between a flowing aqueous phase and a stationary nitrobenzene phase for the voltammetric determination of chloride and nitrate.

Albery et al. ${ }^{328}$ used a novel rotating diffusion cell (RDC) technique, to measure the transfer of carboxylic acids and carboxylates across two membrane systems: a 1.2 $\mu \mathrm{m}$ Millipore MF mixed cellulose filter with an organic phase comprising of a 33 : $33: 33: 1$ mixture by volume of dioxan, dichloroethane, hexane and water and a 1.2 $\mu \mathrm{m}$ Millipore Duralon filter containing hexafluoroisopropanol as the organic phase. Partitioning concentrations were measured by measuring the pH or spectrophotometrically. Manzanares et al. ${ }^{329}$ used the same cell type, but introduced potential control by using two large area $\mathrm{Ag} / \mathrm{AgCl}$ electrodes positioned on either side of the interface and controlled the potential with a four electrode potentiostat in a two electrode configuration. This system was analogous to the traditional metallic rotating disc electrode (RDE) technique and was used to examine the transport properties of $\mathrm{TBA}^{+}$across an organic solvent loaded SLM.

Studies of charged membranes such as Nafion are not of great relevance to the present work. However, mention should be made of the work by Samec et al ${ }^{330}$ for useful experimental details for examining membrane transport processes.

### 6.2 Results

The present work comprised firstly a study of separations in single membrane cells, secondly an investigation of the behaviour of a dual membrane cell and finally, the application of the above to the study of the performance of an engineered dual membrane extraction module constructed at EPFL, Switzerland. The separation of $\left[\mathrm{PtCl}_{6}\right]^{2-}$ and $\left[\mathrm{AuCl}_{4}\right]^{-}$was investigated. Early measurements in the flow cell yielded complicated and poorly resolved voltammetry. Therefore, preliminary voltammetric measurements were carried out in two other cells, with smaller, better defined cell geometries. All the cells used are described in Chapter 2.

### 6.2.1 Single Membrane Cell Results

Before using the EPFL extraction cell, the voltammetry of the $\left[\mathrm{PtCl}_{6}\right]^{2-}$ and $\left[\mathrm{AuCl}_{4}\right]^{\circ}$ ion transfer system was studied using a single membrane cell separating a water/1,2DCE interface. The cell used was:
$\mathrm{Ag} / \mathrm{AgCl}|10 \mathrm{mM} \mathrm{THACl}(\mathrm{aq})| 10 \mathrm{mM}$ THATPBCl $\mathrm{Cl}_{(1,2 \mathrm{DCE})} \mid$ membrane $\mid$

$$
10 \mathrm{mM} \mathrm{LiCl}_{(\mathrm{aq})}+\mathrm{xmM}\left[\mathrm{PtCl}_{6}\right]_{(\mathrm{aq})}^{2-}+\mathrm{xmM}\left[\mathrm{AuCl}_{4}\right]_{(\mathrm{aq})} \mid \mathrm{AgCl} / \mathrm{Ag}
$$

Figure 6.1 shows the voltammetric response of the cell. The baseline corresponds to that of the base electrolyte used. When $0.250 \mu \mathrm{M}\left[\mathrm{PtCl}_{6}\right]^{2-}$ and $0.250 \mu \mathrm{M}\left[\mathrm{AuCl}_{4}\right]^{-}$
were added to the cell two voltammetric waves with half-wave potentials at +0.28 V and +0.55 V were observed. The peak to peak separation of the first wave was approximately 30 mV , corresponding to the transfer of a species with charge $\mathrm{n}=2$, i.e. the simple ion transfer of $\left[\mathrm{PtCl}_{6}\right]^{2-}$ from the aqueous phase into $1,2-\mathrm{DCE}$, as reported in Chapter 5. Therefore, it can be concluded that $\Delta_{o}^{\omega} \phi_{\phi_{r a n s}}\left[\mathrm{PtCl}_{6}\right]^{2-}$ is not affected by the presence of the membrane. However, the diffusional properties of the platinate anions within the membrane were quite different to those of platinate in the bulk aqueous phase. ${ }^{325}$ A calculation of the diffusion coefficient of $\left[\mathrm{PtCl}_{6}\right]^{2-}$ from the results shown in Figure 6.1 gave a value of $D=5.5 \times 10^{-9} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$ showing that tortuosity effects within the pores determine transport. Similar considerations apply to the transfer of the $\mathrm{AuCl}_{4}^{-}$anion.

The wave centred on +0.550 V had a peak to peak separation of approximately 60 mV and corresponded to the transfer of $\mathrm{AuCl}_{4}{ }^{-}$from the aqueous to the organic phase. A problem occurred with the transfer of chloroaurate; on cycling the potential of the cell, the gold transfer peak became less well defined and eventually the whole voltammogram degraded, with large increases in the current. This was similar to the problem observed for the transfer of $\mathrm{Au}(\mathrm{III})$ transfer across the water/MIBK interface. The reason for this degradation was evident on dismantling the cell, metallic gold was visible as a precipitate on the organic side of the membrane. This can be seen first as the formation of a purple/red film of colloidal gold, and then precipitation of bulk gold in the membrane. The stability of chloroaurate is further discussed in Chapter 7.


Figure 6.1 CV showing a) baseline and b) $0.250 \mathrm{mM}\left[\mathrm{PtCl}_{6}\right]^{2}$ and $\left.0.250 \mathrm{mM}\left[\mathrm{AuCl}_{4}\right]\right]^{\text {in }}$ the cell, sweep rate $=0.020 \mathrm{~V} \mathrm{~s}^{-1}$.

It is probable that the choice of a cellulose dialysis membrane was not a good one as chloroaurate appeared to undergo reaction within the membrane. Work by Lachowicz ${ }^{331}$ reported the extraction of tetrachloroaurate into 1,2-DCE using 1 mM 1,12-di-2-thienyl-2,5,8,11-tetrathiadodecane (TTD), from 1 mM to 1 M HCl solutions of chloroaurate. Transport and extraction of Au (III) across an SLM formed from a Celgard 2500 membrane containing a solution of TTD in mchlorotoluene ${ }^{332}$ resulted in $94 \%$ recovery of the gold for a 50 hour extraction, which demonstrates that a prudent choice of the supporting membrane allows the extraction of chloroaurate. Another problem which cellulose presents as a membrane material is that it is not efficient for keeping the two phases separate. It is suitable for a single day of use, but if the cell is left overnight at either open circuit potential or at an applied potential, water leaches into the organic phase. If this technique is to be developed further, a more hydrophobic membrane would be required.

As mentioned in Chapter 5, $\Delta_{o}^{w} \phi_{\text {trans }}\left[\mathrm{PtCl}_{6}\right]^{2-}=-180 \mathrm{mV}$. When THATPBCl is used as the organic supporting electrolyte, the platinates transfer at the less positive end of the potential window, close to the transfer potential of $\mathrm{THA}^{+}$from the organic to aqueous phase. Therefore, the full potential window available is not being utilised and it is not necessary to use $\mathrm{TPBCl}^{-}$as the organic supporting electrolyte anion, as the potential window required was not so large; it is sufficient to use TPB ${ }^{\text {a }}$ as the organic supporting electrolyte anion. Should this technique be scaled up, the difference in cost might be an important consideration; the cost of NaTPB ( $£ 1.27 / \mathrm{g}$ ) is $3 \%$ that of $\mathrm{KTPBCl}(£ 42.80 / \mathrm{g})$, which makes the cost of supporting electrolytes for platinum extraction experiments much lower.

### 6.2.2 Dual Membrane Cell Results

This cell was described in Chapter 2 and was used to test the voltammetric response of an SLM. The two aqueous phases were separated by a supported liquid membrane (SLM) organic phase. The applied potentials refer to the cell:
$\mathrm{Ag} / \mathrm{AgCl}|\mathrm{W} 110 \mathrm{mMLiCl}|$
membrane $\mid 10 \mathrm{mM}$ THATPB $_{(1,2-\mathrm{DCE})} \mid$ membrane
| 10 mM LiCl W2 $\mid \mathrm{AgCl} / \mathrm{Ag}$

There was no control of the potential difference across either of the membrane interfaces, or control of the potential difference across the organic phase, only with respect to the cell as an whole. Therefore, the potentials quoted correspond to overall cell potential and not the usual Galvani scale.

For liquid/liquid experiments at a single interface, the convention is to hold the potential of the organic phase at zero whilst the potential of the aqueous phase is scanned to a more positive potential; in these experiments, the potential of W1 was held constant, whilst W2 was scanned to potentials positive and negative of W1.

The characteristic voltammetry of the back to back membrane cell was been described by Beriet and Girault ${ }^{333}$ and Kihara et al. ${ }^{312,334,335}$ The observed potential window was that of two back-to-back potential windows. Figure 6.2 shows the possible transfer processes which can take place at the positive (Figure 6.2a) and negative limits (Figure 6.2 b ) of the potential window and Figure 6.3 shows the predicted potential window on the basis of these transfers.
a)

$$
\mathrm{E}_{\mathrm{wl}}=\text { zero }
$$



Aqueous phase W1 membrane Organic phase membrane Aqueous phase W2
b) $\mathrm{E}_{\mathrm{wl}}=$ zero


Figure 6.2 a) Phase w2 polarised positive wrt phase w1.
b) phase w2 polarised negative wrt phase w1.


Figure 6.3 Schematic representation of the predicted potential window for the dual membrane cell and the location of the ion transfers.


Figure $6.4\left[\mathrm{PtCl}_{6}\right]^{2-}$ ion transfer in a dual membrane cell. a) Voltammetric bascline b) Baseline and voltammogram following the addition of $146 \mu \mathrm{M}\left[\mathrm{PtCl}_{6}\right]^{2-}$ to the feed phase. c) $\left[\mathrm{PtCl}_{6}\right]^{2-}$ transfer. d) First sweep following 3 hour polarization of cell at $\mathbf{- 0 . 4 7 5} \mathrm{V}$. e) Addition of a further $146 \mu \mathrm{M}\left[\mathrm{PtCl}_{6}\right]^{2-}$ to the feed phase. 1) Prior to and following a second polarization of the cell of $\mathbf{9 0}$ minutes at $\mathbf{- 0 . 4 7 5} \mathrm{V}$. g) Following the second cell polarization.

Figure 6.4 shows the transfer of $\left[\mathrm{PtCl}_{6}\right]^{2-}$ transfer across a dual membrane cell. The step between (Figure 6.4c) and (Figure 6.4d) is the most important; it can be seen that before cell polarization, there is an ion transfer process at potentials slightly negative to +0.400 V , corresponding to the transfer of $\left[\mathrm{PtCl}_{6}\right]^{2-}{ }_{\mathrm{wl} \rightarrow 0}$ from the feed phase (W1) to the organic phase. Following a three hour polarization at -0.475 V , the wave around +0.400 V diminished and a new wave appeared at approximately 0.075 V . As this transfer process is on the negative side of the potential window it corresponds to a process occurring at the second interface. This was assumed to be the transfer of $\left[\mathrm{PtCl}_{6}\right]^{2-}{ }_{0 \rightarrow \mathrm{ww} 2}$.

The addition of a second volume of stock $\left[\mathrm{PtCl}_{6}\right]^{2-}$ to W 1 (Figure 6.4e) and a further 90 minutes of polarization of the cell at -0.475 V (Figure 6.4 f ) appeared to demonstrate that the $\left[\mathrm{PtCl}_{6}\right]^{2-}$ could be moved from the feed phase (W1) to the stripping phase (W2) under potential control. However, on the basis of the transfer positions of the organic supporting electrolyte cation $\mathrm{THA}^{+}{ }_{0 \rightarrow \mathrm{wl}}$ and the transfer of $\left[\mathrm{PtCl}_{6}\right]^{2-}{ }_{\mathrm{wl} \rightarrow 0}$ at the positive end of the potential window, the $\left[\mathrm{PtCl}_{6}\right]^{2-}{ }_{0 \rightarrow \mathrm{w} 2}$ transfer should be at the same potential relative to the transfer $\mathrm{THA}^{+}{ }_{0 \rightarrow \mathrm{w} 2}$, see Figure 6.5.

Re-examination of Figures $6.4 \mathrm{e}-\mathrm{g}$, show that a small peak occurs at the predicted potential of -0.400 V , this is marked with an asterisk. The origin of the peak at 0.075 V has not yet been explained. However, the peak to peak separation is of approximately 30 mV which would indicate that it is due to the transfer of a doubly charged species.


Figure 6.5 Schematic representation of the predicted transfer potentials for the $\left[\mathrm{PtCl}_{6}\right]^{\mathbf{2}}{ }_{\mathbf{w l \rightarrow 0}}$ and $\left[\mathrm{PtCl}_{6}\right]^{2}{ }_{0 \rightarrow \mathrm{w} 2}$ ion transfers.

The single and dual membrane cells proved useful for characterising the transfer of platinate ions across SLMs. Although the mechanism for the transfer of $\left[\mathrm{PtCl}_{6}\right]^{2 \cdot}$ was not fully explained, the preliminary membrane results indicated that scaling-up the extraction experiments of the platinate system to the EPFL extraction flowcell would be worthwhile.

### 6.2.3 Electrochemical Flowcell Results

The flowcell designed by EPFL was used to test extraction efficiency. The cell was set up was as follows:
$\mathrm{Ag} / \mathrm{AgCl} \mid(\mathrm{Wl}) 50 \mathrm{mM} \mathrm{LiCl}$ volume $225 \mathrm{~cm}^{3} \mid$
membrane $\mid 5 \mathrm{mM}$ THATPB $_{(1,2-\text { DCE })} \sim 30 \mathrm{~cm}^{3} \mid$ membrane

$$
\text { |(W2) } 50 \mathrm{mM} \mathrm{LiCl} \sim 40 \mathrm{~cm}^{3} \mid \mathrm{AgCl} / \mathrm{Ag}
$$

The aqueous feeder phase was recirculated through the compartment W1 using a peristaltic pump and a $500 \mathrm{~cm}^{3}$ reagent bottle as a reservoir. The flow rate was calibrated over three 15 minute periods to be $0.65 \mathrm{~cm}^{3} \mathrm{~min}^{-1}$.

The initial concentration of $\left[\mathrm{PtCl}_{6}\right]^{2-}$ in W1 was $0.1 \mathrm{mM}(19.5 \mathrm{ppm})$ and the initial concentration of Copper was $0.5 \mathrm{mM} \mathrm{CuCl}_{2}(31.8 \mathrm{ppm})$. The cell was polarised for 24 hours in the same manner as for the dual membrane experiments.

The concentrations of platinum and added base metal ions in the feed and stripping phases were measured by atomic absorption spectroscopy (AAS) ${ }^{336,337}$ using a Perkin Elmer model 3110 instrument. The instrument was set to the manufacturers recommended parameters for Pt analysis: the flame used was acetylene/air, with a standard nebuliser. Measured line wavelength $=265.9 \mathrm{~nm}$, slit $=0.7 \mathrm{~nm} .{ }^{338}$ Copper concentrations were measured on the same instrument, using measured line wavelength $=324.89 \mathrm{~nm}$, slit $=0.7 \mathrm{~nm} .{ }^{339}$ Calibration curves for Pt and Cu were measured using standards produced from BDH SpectraSol stock solutions.

Table 6.1 Final EPFL electrodialysis cell concentrations as determined by AAS.

| Sample | $\left[\mathrm{Cu}^{2+}\right] / \mathbf{p p m}$ (Molarity) | $\left[\mathrm{PtCl}_{6}\right]^{2-} / \mathbf{p p m}$ (Molarity) |
| :---: | :---: | :---: |
| Feed Phase, w1 | $23.6 \quad(371 \mu \mathrm{M})$ | $16.3 \quad(83.6 \mu \mathrm{M})$ |
| Organic Phase | $0.54 \quad(8.5 \mu \mathrm{M})$ | $3.0 \quad(15.4 \mu \mathrm{M})$ |
| Strip Phase, w2 | Below L.O.D. | Below L.O.D. |

The platinum concentrations measured by AAS were below the expected level for the organic and the stripping phases and very little ion transfer appeared to have taken place. Problems may have occurred with the method of analysis:

- In the standard method of analysis for platinum, copper is added to enhance the platinum signal. The presence of copper in the $w 1$ phase but not in either $w 2$ or in the organic phase, may have caused discrepancies between the measurements.
- Matrix effects due to the large supporting electrolyte concentration of $\mathrm{LiCl}(50$ mM , and therefore 500 times the concentration of platinum in the starting solution), may have caused significant suppression of the Pt and Cu responses.
- Comparison of samples in different solvents can give rise to inaccurate results.

The analytical facilities available were insufficient to solve these problems. Comparing the initial concentrations of $\mathrm{Pt}_{\mathrm{wl}}(100 \mu \mathrm{M})$ and $\mathrm{Cu}_{\mathrm{wl}}(500 \mu \mathrm{M})$ with those found in the organic phase $\mathrm{Pt}_{\text {org }}(15.4 \mu \mathrm{M})$ and $\mathrm{Cu}_{\text {org }}(8.3 \mu \mathrm{M})$; from an initial $\mathrm{Pt}: \mathrm{Cu}$ ratio of $1: 5$, the concentration in the organic phase after 24 hours was $2: 1$. This is a reversal in concentration of $10: 1$ for the extraction of Pt over Cu into the organic phase. However, the fact that no significant concentration of Pt was detectable in the stripping phase means in terms of the desired extraction, that this experiment cannot be considered to be successful. It is possible that in order to preserve electroneutrality during the $\mathrm{Pt}(\mathrm{IV})$ transfer a corresponding counter ion transfer to or from the SLM must take place. It was expected that due to the base electrolyte ratio, that the ionic concentration in the membrane would have self-adjusted to the appropriate value, thus allowing unhindered $\mathrm{Pt}(\mathrm{IV})$ transfer. A possible reason for the absence of significant extraction could have been salt precipitation in the
membrane due to forcing salt transport to preserve electroneutrality when $\left[\mathrm{PtCl}_{6}\right]^{2-}$ is transferred.

Unfortunately, the number of experiments which could be carried out was limited by the time available, had further experiments been possible, the following points would have been addressed in order to ascertain whether the under-performance of the extraction of $\left[\mathrm{PtCl}_{6}\right]^{2-}$ was due to the device or to the cell concentrations.

- The thickness of the aqueous chamber $(0.6 \mathrm{~cm})$ may have had a large effect upon the efficiency of the extraction. For the flow rates used $\left(0.65 \mathrm{~cm}^{3} \mathrm{~min}^{-1}\right)$ with a chamber volume of $32.5 \mathrm{~cm}^{3}$, the solution had an approximate residence time in the chamber of 50 minutes. In Table $5.4, \mathrm{D}_{\mathrm{PtCl} 6}$ is given as $4.7 \times 10^{-6} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$, in 50 minutes $\left[\mathrm{PtCl}_{6}\right]^{2-}$ could be expected to diffuse through approximately 0.014 cm , which is much less than the thickness of the aqueous chamber. ${ }^{340}$ Decreasing the thickness of the chambers may have enhanced the stripping efficiency.
- Poor mass transport in the organic phase, this could be have been prevented by recirculating the solvents in the organic chamber and the stripping phase.
- The stability of the ion-pair formed between $\left[\mathrm{PtCl}_{6}\right]^{2-}$ and the $\mathrm{THA}{ }^{+}$in the organic phase, as discussed in the previous Chapter, may have caused the stripping step to be energetically unfavourable. This may have been overcome by reducing the volume of the organic phase, so that the amount of $\mathrm{THA}^{+}$ required was lower, perhaps by use of a single organic solvent impregnated membrane instead of a dual membrane supported organic phase.
- Increasing the stripping time, the current density and the counter electrode areas may all have improved the extraction performance of the cell.


## 7 Formation of Gold Nanoparticles by Reduction With Ketones

This Chapter describes a group of observations on the reduction of Au (III) by ketones, which were regarded as prime candidates for the organic phase in electroassisted metal ion extraction.

### 7.1 Reduction of Au(III) by MIBK

The main oxidation states of gold are $A u(I)$ and $A u(I I I)^{341}$ although $A u(I I)$ has been reported. Gold(III) gives square planar chloroaurate anions, ${ }^{342,343}\left[\mathrm{AuCl}_{4}\right]^{\circ}$, which are stable in acidic solution. ${ }^{344}$ As mentioned in Chapter 5, the reversible ion transfer of $\left[\mathrm{AuCl}_{4}\right]^{-}$across the water/1,2-DCE interface occurs at $\Delta_{0}^{w} \phi=+0.110 \mathrm{~V}$. However, when methylisobutyl ketone (MIBK) was used as the organic solvent, [ $\left.\mathrm{AuCl}_{4}\right]^{-}$ transfer was no longer reversible.

It was observed that the $\left[\mathrm{AuCl}_{4}\right]^{-}$ion transferred to the organic phase was rapidly reduced in the interfacial region and eventually a gold coloured precipitate appeared at the bottom of the cell. The precipitate was filtered and washed with abundant water. After vacuum drying the gold content was approximately $91 \%$ as determined by microanalysis, showing that a significant amount of organic adsorbate was present.

The reduction of $\left[\mathrm{AuCl}_{4}\right]^{-}$in the absence of an applied potential was also observed, both in the presence and in the absence of base electrolytes. These experiments were carried out by contacting the phases overnight and using $1 \mathrm{mM}\left[\mathrm{AuCl}_{4}\right]^{-}$in the aqueous phase. After contact, a gold film was visible at the interface.
[ $\left.\mathrm{AuCl}_{4}\right]^{-}$is known to partition from water into ketone solvents and this extraction is utilised in analytical techniques using a MIBK preconcentration step prior to elemental analysis. ${ }^{169,170}$ The transfer can be followed by the clear changes in colour when an aqueous solution of $\left[\mathrm{AuCl}_{4}\right]^{-}$(yellow) is brought into contact with an immiscible ketone (colourless).

The possible redox reactions of $\mathrm{Au}(\mathrm{III})$ which can lead to reduction to metal ${ }^{345}$ are:

| $\left[\mathrm{AuCl}_{4}\right]_{(\mathrm{aq})}+3 \mathrm{e}^{-} \hookrightarrow \mathrm{Au}_{(\mathrm{s})}+4 \mathrm{Cl}^{-}$ | $\mathrm{E}^{0}=+1.002 \mathrm{~V}$ |
| :--- | :--- |
| $\mathrm{Au}^{3+}+2 \mathrm{e}^{-} \hookrightarrow \mathrm{Au}^{+}$ | $\mathrm{E}^{0}=+1.401 \mathrm{~V}$ |
| $\mathrm{Au}^{3+}+3 \mathrm{e}^{-} \hookrightarrow \mathrm{Au}_{(\mathrm{s})}$ | $\mathrm{E}^{0}=+1.498 \mathrm{~V}$ |

$\mathrm{Au}(\mathrm{II})$ disproportionates in a similar manner to $\mathrm{Cu}(\mathrm{I})$, to $\mathrm{Au}(\mathrm{I})$ and $\mathrm{Au}(\mathrm{III}){ }^{346}$ Also $\mathrm{Au}(\mathrm{I})$ is known to disproportionate to $\mathrm{Au}(\mathrm{III})$ and $\mathrm{Au}(0):{ }^{347}$

$$
\begin{equation*}
3 \mathrm{Au}^{+} \leftrightharpoons \mathrm{Au}^{3+}+2 \mathrm{Au}_{(\mathrm{s})} \quad \mathrm{K} \approx 10^{10} \tag{7.4}
\end{equation*}
$$

Experiments were conducted to test the reactivity of $\left[\mathrm{AuCl}_{4}\right]$ in the presence of organic solvents that could be used in electroassisted solvent extractions. $5 \mathrm{~cm}^{3}$ aliquots of $5 \mathrm{mM}\left[\mathrm{AuCl}_{4}\right]^{-}$in water were stirred continuously with $2.5 \mathrm{~cm}^{3}$ of the organic solvent for 24 hours. From this preliminary work, summarised in Table 7.1, it became apparent that the reduction of $\left[\mathrm{AuCl}_{4}\right]$ was caused by the ketone solvent itself.

Davies and Lewis ${ }^{348}$ made similar observations in Liverpool in the first half of this century and synthesised gold nanoparticles using acetone as a reducing agent. Their preparation method was as follows: $480 \mathrm{~cm}^{3}$ redistilled water, $5 \mathrm{~cm}^{3}$ of a $1.2 \%$ gold chloride solution, $14 \mathrm{~cm}^{3}$ of 0.09 M potassium carbonate solution and $3 \mathrm{~cm}^{3}$ of acetone were brought to the boiling point and allowed to boil vigorously for three minutes. A faint pink colouration appeared on heating, turning to deep ruby-red on further heating. Similar experiments were carried out by Turkevich et al. ${ }^{349}$

If the aqueous phase is discarded following extraction of $\left[\mathrm{AuCl}_{4}\right]^{-}$into the ketone, as is usual in the analytical techniques, $\left[\mathrm{AuCl}_{4}\right]^{-}$is stable in the ketone phase for periods of weeks or longer. However, if the aqueous phase is left in contact with the organic phase following the transfer, $\mathrm{Au}(\mathrm{III})$ is reduced to $\mathrm{Au}(0)$, forming a gold mirror/film at the interface, in most cases within 24 hours. The formation of the gold film was followed ellipsometrically. ${ }^{350}$ A clear change in the ellipsometric angles $\Delta$ and $\Psi$ can be seen on the addition of $\left[\mathrm{AuCl}_{4}\right]^{\circ}$ to the cell (Figure 7.1).

The negative slope observed in this Figure is characteristic of growth of a film at the interface. However, the slope observed of -4.88 could not be fitted (Ellgraph Software, Southampton) to model calculations using the bulk optical constants of gold, which are known to differ markedly from those of nanostructured materials. ${ }^{351}$

Although it is not possible to make a proper fit from these experiments, the $\Delta-\Psi$ dependence corresponded to values of the refractive index much greater than those of bulk gold, as is known to be the case for nanoparticles. ${ }^{351}$

Table 7.1 Reactivity of 5 mM aqueous $\mathrm{AuCl}_{4}{ }^{-}$with organic solvents.

| Solvent | Observation |
| :---: | :---: |
| Acetone | Miscible with water, flakes of gold were observed |
| MIBK | Gave the same ppt. of Au as previously observed for MIBK |
| 2-Octanone |  |
| 2-Nonanone |  |
| Toluene | No uptake of $\mathrm{AuCl}_{4}{ }^{\circ}$, no precipitate was observed |
| Diethyl ether | Immiscible with water, no precipitate was observed |
| Ethyl Acetate | Immiscible, slight uptake of [ $\left.\mathrm{AuCl}_{4}\right]^{\prime}$, no precipitate |
| 1,2-DCE | Immiscible, no uptake of [ $\left.\mathrm{AuCl}_{4}\right]^{\prime}$, no precipitate |
| Acetonitrile | Miscible with water, no precipitate was observed |



Figure $7.1 \Delta-\Psi$ signature for the spontaneous growth of gold films at the MIBK / aqueous $\left[\mathrm{AuCl}_{4}\right]^{-}$interface.

### 7.2 Gold Nanoparticle Formation

The rate of reduction is accelerated if the phases are mixed for a brief period and then allowed to separate and the formation of an interfacial metal film can then be observed. However, if the phases are mixed continuously by mechanical stirring, the reduction can occur in as little as 2 hours and the purple colour observed in the lower aqueous phase was indicative of gold nanoparticle formation. The reduced gold eventually formed a fine powder that settled and agglomerated into pellets.

The reduction of $\mathrm{Au}(\mathrm{III})$ to $\mathrm{Au}(0)$ was observed at different concentrations of the aqueous chloroaurate solutions ranging from 0.1 to 30 mM . The particles formed are only stable for 24 to 48 hours depending on the initial concentration of $\mathrm{AuCl}_{4}{ }^{\circ}$ used. No protecting groups have been used for this work and no attempt was made to ligand stabilise the particles.

The reduction of $\mathrm{Au}(\mathrm{III})$ to $\mathrm{Au}(0)$ at the water/solvent interface requires a reducing $=$ agent. In the phase transfer method of Brust et al. ${ }^{352,353}$ sodium borohydride was used. In the present system the only species that could react with the chloroaurate was the ketone. If the ketone was acting as the reducing agent it must, in turn, be oxidised. There are few reports in the literature for the oxidation of ketones: one rare example is the use of vanadium oxide to oxidise butan-2-one to 2,3-butanedione. ${ }^{354}$

### 7.3 Reaction Mechanism

It is not generally known that ketones can act as reductants for chloroaourate. It is proposed that in the present case, the reducing agent is the enol form of the ketone.

There are some examples of this reactivity in the literature. For example, the enol form of methyl ethyl ketone is known to react with molecular oxygen to form ethanoic acid and ethanal. ${ }^{354}$ The chemistry of ketones is strongly dependent on the keto-enol tautomerism, an example of which for MIBK is given in (7.5): ${ }^{355 \mathrm{a}}$


MIBK Ketone MIBK Enol form

It is proposed that the enol form is the reducing agent and that the double bond is oxidised by the chloroaurate anion. The course of the reaction probably bears similarities with the use of $\mathrm{Cu}(\mathrm{II}), \mathrm{Mn}$ (III) or $\mathrm{Ce}(\mathrm{IV})$ as a redox trap for nucleophilic alkyl radicals. ${ }^{356}$ A proposed reaction mechanism is given in (7.6). Here the enolate oxygen may complex with gold and the radicals resulting from electron transfer could then follow two pathways: i) formation of a carbon-carbon bond between two radicals, or ii) a.redox reaction where the radical is oxidised by $\mathrm{Au}(\mathrm{III})$ which is reduced to $\mathrm{Au}(\mathrm{II})$.


Further reduction by the radical or subsequent disproportionation reactions of Au (II) and $\mathrm{Au}(\mathrm{l})$ to $\mathrm{Au}(0)$ could occur via the mechanism (7.7) below.


Another possibility is to consider a mechanism analogous to that in the iodoform reaction, ${ }^{355}$ which would involve the keto/enol tautomerism step. The iodoform reaction is specific to secondary 2-alkanols containing the structural unit $\mathrm{RCH}(\mathrm{OH}) \mathrm{CH}_{3}$ and therefore it is also specific to methyl ketones. Secondary 2-
alkanols are attacked by iodine in aqueous sodium hydroxide. However, in the present case, gold is present in the form of the acid salt $\mathrm{HAuCl}_{4}$ and so the pH should not be conducive to the iodoform reaction.

At room temperature the keto-enol equilibrium in Scheme 7.5 lies to the left, the enol being present only as a fraction of a percent and the reaction kinetics would be determined by the rate of tautomerisation. The oxidation products following electron transfer are unknown. The equilibrium between the ketone and the enol is shifted towards the right especially since the aqueous phase was acidic in the present experiments. This explains why the reduction of chloroaurate only occurs when both the ketone and water are present, i.e. at the liquid/liquid interface. Supporting evidence for this are the results by Matsuda et al. ${ }^{357}$ and Held and Pratt ${ }^{358}$ who used spectroscopic techniques to study the effect of hydrogen bonding on the keto-enol - tautomerism in clusters of 2 -pyridone and water, between the amine hydrogen and the carbonyl oxygen. In addition, Meot-Ner et al. ${ }^{359}$ modelled membrane transport processes and reported strong interaction and cluster formation in the water/acetone and water/diketone systems.

The reduction mechanism for chloroaurate proposed proceeds via a keto-enol tautomerism to an alkyl radical which may then reduce the chloroaurate. The reaction products other than $\mathrm{Au}(0)$ are not yet known.

### 7.4 UV Visible Spectroscopy and TEM Images

Gold nanoparticles give a characteristic plasmon absorption in the UV/visible spectrum. ${ }^{360}$ For small gold clusters the plasmon absorption has a maximum close to 530 nm . For larger nanoparticles, the wavelength is shifted slightly towards the red end of the spectrum, closer to 560 nm . Therefore it is possible to follow qualitatively the size of the particles obtained with various initial concentrations of $\left[\mathrm{AuCl}_{4}\right]^{-}$in the aqueous phase. Figure 7.2 shows the spectra of the MIBK phase for different initial concentrations of $\left[\mathrm{AuCl}_{4}\right]^{-}$in the aqueous phase. The maximum of the plasmon band is shifted to longer wavelengths for particles formed from higher concentrations of $\left[\mathrm{AuCl}_{4}\right]^{-}$(Table 7.2).

The 3.0 mM sample had an opaque golden colour, similar to a suspension of gold powder when viewed from the same side as the light source. However, on direct transmission, the solution appeared to be totally transparent and purple in colour. Some agglomeration was evident from light scattering observations, which lead to an apparent decrease in absorbance.

In order to try to understand the unusual light dispersion properties of these preparations transmission electron microscopy (TEM) ${ }^{352,361-363}$ images were taken to determine size distribution. The TEM image (Figure 7.3) shows that both large and small particles are present, indicating a bimodal size distribution of nanoparticles of 2-10 nm diameter (Figure 7.4) and clusters of nanoparticles of diameter in the range $30-70 \mathrm{~nm}$ (Figure 7.5). The unusual colours of the solution and the light dispersion effects are related to the presence of the different sizes.

Table 7.2 Dependence of $\lambda_{\text {max }}$ on the initial concentration of $\mathrm{AuCl}_{4}{ }^{-}$in the aqueous phase.

| $\left[\mathrm{AuCl}_{4}\right] / \mathrm{mM}$ | $\lambda_{\text {max }} / \mathrm{nm}$ |
| :---: | :---: |
| 0.5 | 532 |
| 1.0 | 550 |
| 2.0 | 560 |
| 3.0 | 566 |



Figure 7.2 UV/Visible absorption spectra of ketone nanoparticles with increasing concentration of $\mathrm{AuCl}_{4}^{-}$in the aqueous phase. a) 0.5 mM, a) $\left.1.0 \mathrm{mM}, ~ a\right) ~ 2.0 \mathbf{~ m M}$ and d) $\mathbf{3 . 0} \mathbf{~ m M}$.


Figure 7.3 Clusters of Au nanoparticles formed from $0.75 \mathrm{mM} \mathrm{AuCl} \mathbf{H}_{4}$. Large nanoparticles diameter 30-50 nm (left) and small nanoparticles diameters 2-10 nm (right).


Figure 7.4 Magnified image of clusters of large Au nanoparticles diameters $30-50 \mathrm{~nm}$.


Figure 7.5 Magnified image of smaller nanoparticles nanoparticles, diameters 2-10 nm.

Examination of the electron diffraction patterns can yield information about the crystal structure of the sample. ${ }^{364}$ A polycrystalline sample normally produces a diffraction pattern of well defined rings, a single crystal would give a spot pattern. Figure 7.6 shows a pattern which is half way between a ring pattern and a spot pattern, this is characteristic of the diffraction given by superimposed multiple spot patterns given by several independently oriented crystals.

A comparison of the ring ratios with the reciprocal of the plane spacing, can be used to confirm the crystal structure, for a cubic system the distance between adjacent planes, d is given by:
$\frac{1}{d^{2}}=\frac{h^{2}+k^{2}+l^{2}}{a}$

Table 7.3 shows the calculated values of $1 / \mathrm{d}$ of the allowed reflections for gold, a face centred cubic (FCC) solid, ${ }^{365}$ also given are the radii of the ring/spot patterns taken directly from the photographic negative of the diffraction pattern. A comparison of the ratios of the values of $1 / d$ to the value of $1 / d_{111}$ with the ratios of the ring radii, $r$, to the smallest ring radius, $r_{111}$ showed good correlation. Five crystallographic planes were identified, the 200 plane was not identifiable, however, this can be attributed to an overdeveloped negative. These measurements provide good evidence that the sample was polycrystalline or multicrystalline and of FCC structure, indicative of a metallic gold structure.

### 7.5 Conclusion

Contrary to expectations from the analytical literature, ketones act as reducing agents for $\mathrm{Au}(\mathrm{III})$ when water is present. The size of the particles formed appear to follow a bimodal distribution. For practical applications in electroassisted separations, ketones cannot be used as the liquid membrane phase due to their reactivity with Au (III). The interfacial growth phenomenon observed is worthy of a further investigation as an example of nucleation and growth of a metallic film at a liquid/liquid interface.

Table 7.3 Analysis of electron diffraction ring patterns.

| HkI | $\mathbf{d}$ | $\mathbf{1 / d}$ | $\mathbf{1 / d}$ ratio | Ring No. | Radius | Ratio | hkl $\sqrt{ }$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 111 | 0.235 | 4.26 | - | 1 | 18 | - | - |
| 200 | 0.204 | 4.90 | 1.15 | 2 | 26 | 1.44 | $?$ |
| 220 | 0.144 | 6.94 | 1.63 | 3 | 30 | 1.66 | $\checkmark$ |
| 311 | 0.123 | 8.13 | 1.91 | - | $\ddots$ | - | $\times$ |
| 222 | 0.117 | 8.55 | 2.01 | 4 | 41 | 2.05 | $\checkmark$ |
| 400 | 0.102 | 9.80 | 2.30 | - | - | - | $\times$ |
| 331 | 0.093 | 10.75 | 2.53 | 5 | 46 | 2.55 | $\checkmark$ |
| 422 | 0.083 | 12.05 | 2.83 | 6 | 51 | 2.83 | $\checkmark$ |
| 333 | 0.078 | 12.82 | 3.01 | 7 | 55 | 3.00 | $\checkmark$ |



Figure 7.6 TEM electron diffraction pattern for gold nanoparticle sample

## 8 Conclusions and Future Work

### 8.1 Conclusions

The aim of this project was to produce a selective extraction system for the separation of precious metal ions from waste electrolyte streams utilising liquid/liquid electrochemical techniques. Although this task was not fully achieved, progress has been made in several areas which show that such a separating system may be achieved.

Some fundamental physicochemical properties of liquid/liquid systems were explored. For electron transfer reactions the dependence of the rate of electron transfer on supporting electrolyte concentration in the organic phase has been measured using electrochemical impedance spectroscopy for the water/1,2-DCE interface. No dependence of the rate of electron transfer on the concentration of the supporting electrolyte in the organic phase was observed. The effect of the solvent on the kinetics of electron transfer has also been examined with results showing that the expected Marcusian dependence is not observed.

It should be noted that the results for the kinetic studies of ET are the result of a single electrochemical technique, it would be useful if the same systems could be studied using a second technique,in order to confirm the validity of the data, the obvious choice would be by the use of SECM, ${ }^{53-56}$ however, that technique was not available in Liverpool.

Following the recent work of Quinn et al. ${ }^{134}$ the experimental conditions which had up to now been assumed to allow the study of heterogeneous electron transfer reactions are being questioned. The ET has been assumed to occur via a simple outer sphere mechanism, where there are no accompanying chemical reactions.

Although the present work does not share the pessimistic view of Quinn, it has to be conceded that the redox couples and solvents might be examined more critically than in previous studies. For example the use of TCNQ as the organic redox couple will give a reversible electrochemical response at a microelectrode in 1,2-DCE. ${ }^{54}$ Also, TCNQ is highly hydrophobic and does not readily transfer to the aqueous phase. However, the lithium salt of the $\mathrm{TCNQ}^{-\quad}$ radical anion is readily dissolved in water. In addition, the radical anion can form a dimer in some solvents. ${ }^{366,367}$

In the present work $1 \mathrm{M} \mathrm{Li}_{2} \mathrm{SO}_{4}$ has been employed. The formation of the TCNQ ${ }^{-}$ radical at the interface in the presence of excess of $\mathrm{Li}^{+}$provides ideal conditions for interfacial ion pair formation. It may then be possible for the water soluble ion pair to partition to the aqueous phase.

In the case of the dimerization of $\mathrm{TCNQ}^{\circ}$, an equilibrium mixture of (TCNQ $\left.{ }^{\circ}\right)_{x}$ and a dimeric complex $\left(\mathrm{TCNQ}_{2}{ }^{2-}\right)_{x}$ was observed on the reduction of adsorbed films on platinum electrodes. ${ }^{368}$ In addition, in a UV-visible spectroscopic study, evidence was given for the dimerization of TCNQ ${ }^{-6}$ in aqueous solutions. ${ }^{366}$ In the same study other solvents were used including n-methylformamide $\left(\mathrm{HCONHCH}_{3}\right)$ with a dielectric permittivity higher than water, $\left(\varepsilon_{\mathrm{HCONHCH}}=189\right)$, methanol and acetonitrile were also used. No detectable dimerization was found in the other
solvents at room temperature, the authors concluded that specific solvation effects were important in the determining the stability of the dimer. As several novel solvents have been used in the present study, it would be interesting to further investigate this effect.

Several solvents previously unused for liquid/liquid studies have been screened for their use; one solvent in particular, o-difluorobenzene (o-DFB) shows great promise for future work.

The ion transfer studies show that platinates can be separated under potential control across the water/1,2-DCE and the water/MIBK interfaces. Ion transfer and separation of chloroaourate and chloroplatinates have been discussed on the basis of the galvani potential of ion transfer. Evidence of ion-pairing between the platinates and the organic supporting electrolyte cation was found. The thermodynamics of the platinate transfer have also been explored and in collaboration with Dr Robert Deeth, preliminary density functional theory calculations have been performed to explain the experimental results in terms of a model accounting for the surface charge density of the platinates. This goes beyond the classical Born approach of treating the ion as a hard sphere of charge in a dielectric continuum.

A selective electroassisted extraction of metal ions across dialysis membranes was attempted using both single and dual membrane supported liquid/liquid interfaces for separating the platinates from base metals. $\left[\mathrm{PtCl}_{6}\right]^{2-}$ transfer across a supported liquid membrane was demonstrated. The scale-up experiments were not successful, but if
certain key points can be addressed, it may be possible for future studies to build on what has been achieved here.

In addition to the traditional liquid/liquid work, a method for preparing gold nanoparticles has been found. The reductive effect of ketones on tetrachloroaurate at the water/ketone interface has been studied using several techniques. The formation of gold mirrors at the interface was observed and nanoparticles have been isolated and characterised.

### 8.2 Recommendations for Future Work.

For ET studies, it should be noted that although a 10 mM concentration of supporting electrolyte provided the best impedance response in $1,2-\mathrm{DCE}$, this concentration is not necessarily the best to use for all solvents. Ideally, similar concentration dependence experiments should be carried out for each of the novel solvents examined, this task was beyond the scope of the present work.

For the evaluation of the Marcusian term of the new solvents in section 3.5, the values of $n$ and $\varepsilon$ for the $m$-DFB/1,2-DCE mixture were estimated by averaging the values for the component solvents. The refractive indices for those two solvents were similar, 1.444 and 1.438 respectively, therefore the deviation from the true refractive index of the mixture should be small. The dielectric permittivities of the component solvents, however, were quite different, 5.01 and 10.44 respectively. Therefore the deviation of the real value of the dielectric permittivity of the $m-D F B /$ 1,2-DCE mixture, from the estimated value of 7.71 may be quite large. The real value could be obtained from capacitance measurements. ${ }^{86}$

The reactivity of the organic solvent should be carefully considered, the present work has demonstrated that platinates can be transferred across the water/MIBK interface however, chloroaurate undergoes a spontaneous reduction at the same interface. Yang et al. ${ }^{369}$ reported that the voltammetry of nitrobenzene on Au single crystals was strongly dependent on the surface crystallographic orientation and that the nitrobenzene undergoes electroreduction under acidic conditions. Whilst it is accepted that the liquid/liquid interface lacks the stable surface structure and geometry which gives rise to the electrocatalytic activity characteristic of metallic electrodes, with specific conditions electrochemical reactions can occur at the liquid/liquid interface. Cunnane and Evans have recently demonstrated that the liquid/liquid interface can be used to conduct controlled electropolymerisation, ${ }^{370}$ therefore the susceptibility to redox reactions of the new solvents used in the present work should be carefully considered.

The lack of suitable redox switchable ligands for testing for use in electroassisted separations was mentioned earlier, however from the results obtained with the commercially available ligand N,N-dimethylaminomethylferrocene (DMAMF), it would be interesting to further explore this topic with other redox switchable ligands.

There is great interest in the use of platinum compounds as anti-cancer agents, ${ }^{371}$ examples such as cisplatin and carboplatin were mentioned in Chapter 5. Some tumours are resistant to cisplatin, alternative platinum complexes are being sought which can offer similar therapeutic properties. ${ }^{372}$ Berners-Price et al. ${ }^{373}$ reported the anti-tumour activity of $\mathrm{Ag}(\mathrm{l})$ and $\mathrm{Au}(\mathrm{I})$ pyridyl phosphine complexes against human
ovarian carcinoma cells, the results showed a correlation between the degree of antitumour selectivity and the water/octanol partition coefficients.

Water/octanol studies are often used as a measure of the ability of a drug to cross a cell membrane, liquid/liquid electrochemistry could present a way of screening ionisable drugs to test their ability to cross cell membranes. ${ }^{109}$ Allsopp et al. ${ }^{374}$ studied the susceptibility of carboplatin in aqueous solution to nucleophilic substitution. The reactions were studied at elevated temperatures and in the absence and presence of $\mathrm{Cl}^{-}, \mathrm{SCN}^{-}, \mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}, \mathrm{N}_{3}{ }^{-}$and $\mathrm{I}^{-}$. It was suggested that the degradation of carboplatin gave rise to some charged intermediates.

Cheng et al. ${ }^{244}$ found that pH can also have a large effect on $\Delta_{0}^{w} \phi_{\text {rans }}$ for both $\left[\mathrm{PtCl}_{6}\right]^{2-}$ and $\left[\mathrm{PtCl}_{6}\right]^{2-}$. It is also likely that the anti-cancer compounds in use today can be ionised by changing pH . It would be interesting to use the methodology established by Girault et al. ${ }^{375}$ to measure the pH dependence of $\Delta_{0}^{w} \phi_{\text {rans }}$ of such anticancer compounds.

The directions which could be followed for the molecular modelling of the platinates are numerous, the DFT modelling of solvated ions and calculation of surface charge would be useful for elucidation of the influence of the ligand and solvent on $\Delta_{0}^{w} \phi_{\text {rans }}$. A measure of the ratio of axial to equatorial radii-for the-square planar platinates should be obtainable from DFT calculations, this would enable the use of the StokesEinstein equation ${ }^{86,246}$ for the prediction of the diffusion coefficients of these ions.

For the scale up of the electroassisted separation technique, it was mentioned in Section 6.2.1 that the dialysis membrane was water permeable, this allowed significant leaching of the aqueous phases into the organic chamber, which may have had an effect on the analysis of Cu and Pt by AAS. For any future studies an alternative membrane material must be identified.

Problems with gold plating out onto the membranes could be overcome if a suitable membrane material is found. From the literature available, this should be easily achievable. The analytical method used for the analysis of Pt concentration by AAS was clearly of insufficient sensitivity. The validation of a suitable method for trace analysis of Pt in solution would be of use for future studies. ${ }^{175,376-379}$

For the gold nanoparticle work a natural progression would be to attempt to ligand stabilise the particles in order to increase their lifespan beyond 48 hours.

## Appendix




| quency | 2* $\mathbf{z r}^{\mathbf{*}}$ | 2/cm ${ }^{2}$ | 2"icm ${ }^{2}$ | R | C'R |  |  |  | r. |  | r | r'm |  |  | ) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $2000+03$ | 68SE+03 3 75E+02 | 77 | - 268.01 | OOE | 30 | 70E | 34E-02 | $126 \mathrm{E}+04$ | 2436 | $200 E-03$ |  |  |  |  |  |
| $1596+03$ | 686E $032383 E+02$ | $778 E+02$ | 321 EtOT |  | $267 \mathrm{E}+\infty$ | -2 57E-03 | $3006-02$ | $\bigcirc$ | ${ }^{3} 886 E^{-03}$ | $\begin{aligned} & -20 E-03 \\ & -4 E 3 E-3 \end{aligned}$ | $\begin{aligned} & -193 E-0 \\ & -307 E-0 \end{aligned}$ | $\begin{aligned} & -16 E-07 \\ & -1 ~ a \in-07 \end{aligned}$ | $\begin{gathered} 892 \mathrm{E}-03 \\ 1006.02 \end{gathered}$ | $237 E+02$ $-101 E+02$ |  |
| $126 E+03$ | 806E+033 $208 E+02$ | ${ }_{7} 7 \mathrm{TE}+09$ | $236 \mathrm{E}+01$ |  | -201E $+\infty 0$ | 3 64E-03 | $421 \mathrm{E}-02$ | 7 23E+ | -33E.03 | -1 19E-92 | -1 OSE-0 | -1 SOE-08 | $100 E-12$ $112 \mathrm{E}-22$ | -1 OEE | -1.28EC02 |
| $100 \mathrm{E}+03$ | $687 \mathrm{E}+0331.44 \mathrm{E}+02$ | $779 E+02$ | -1 $63 E+01$ |  | -1 $13 \mathrm{E}+00$ | - 06E-0 | $507 \mathrm{E}-02$ |  |  | -311E.02 |  |  |  |  |  |
| $786 E+02$ | $5 \mathrm{B7E}+03 \mathrm{~S} 93 \mathrm{E}+01$ | $7796+02$ | -101E+01 |  | $-113 \mathrm{E}+\infty$ | -1 DoE | + 75E-02 | 8006 | -1 12E-01 | - 209 E | - 224 E 20 | -5 E9E-08 | 1.28E.02 |  | $-200 E+01$ $-317 E+\infty$ |
| $632 \mathrm{E}+02$ | $680 \mathrm{E}+033$ 37E+01 | 7.80E+02 | -16E+00 |  | - GAEP | $374 \mathrm{E}-02$ | $234 \mathrm{E}-\mathrm{O}$ | $397 E+0$ | ${ }^{1} 11 \mathrm{E} 02$ | 4 42E.01 | $224 E-05$ 229605 |  | 141E-02 | -1.31E+00 |  |
| $502 \mathrm{E}+02$ | $6885+033-73 E+\infty 0$ | $780 \mathrm{E}+02$ | $766 E-97$ |  | $167 \mathrm{E}-22$ | $205 E-02$ | 1 30E+00 | $316 E+0$ | -1.11E-03 | -1.22E+C0 | 2236505 3 S3E-07 | 114E-04 | 1 S0E-02 | A47E-01 | $217 E 600$ <br> 21E-09 |
| $399 E+02$ | $689 E+03-501 E+01$ | 7 11E+02 | $568 \mathrm{E}+\infty$ |  | 6 40E.OY | $1.96 E-02$ | 174 E .01 | $251 \mathrm{E}+03$ |  | $116 E-01$ |  |  |  |  |  |
| $317 \mathrm{~F}+02$ | $6906+03$ \& 31E+01 | $782 \mathrm{~F}+02$ | $106 E+01$ |  | $162 \mathrm{E}+\infty$ | $142 \mathrm{E}-02$ | $0.25 \mathrm{E}-02$ | $1996+\infty$ | 162 E -.33 | - 512 E -02 | ${ }_{762 \mathrm{E}}^{227}$ | - 4 HIEE-06 | $2006-02$ 224602 | S07E-02 | +46E 900 |
| $252 \mathrm{E}+02$ | 691E+03 -1 37E+02 | $7836+02$ | $155 \mathrm{E}+01$ |  | $285 E+\infty$ | 1.15E-02 | 8.25E-02 | 1.58E +03 | 1.74E-.03 |  | 1 10EE | -2 1 18EE05 | 224102 $2515-02$ |  |  |
| $2006+02$ | $692 \mathrm{E}+03 \mathrm{-1} 82 \mathrm{E}+02$ | 7 PME +02 | $207 \mathrm{E}+01$ |  | $402 \mathrm{E}+0$ | 9 08E-03 | 4 S6E-02 | 1.26E+03 | $216 \mathrm{E}-03$ | -214E-02 | 1.r2E-® | -1 171 ERES | $2.51 E-02$ $282 E-02$ | l $81 \mathrm{E}+\infty$ $46 \in E+\infty$ | $322 E+01$ $-62 E+01$ |
| $1596+02$ | 693E+03 2.35E+02 | 7 85E+02 | 2 67E |  | 5.20E+00 | 703E-03 | 361 E-02 | 9 98E+02 |  |  |  |  | $3.17 E=0$ |  |  |
| $1.26 E+02$ | $693 \mathrm{E}+03302 \mathrm{~S}+02$ | 78SE+CO | 3 43E+09 |  | $8006+00$ | \$03E-03 | $203 E-02$ | 7 93E 022 |  | -100E-02 | 2. | -1 30E06 | $3.17 E 02$ 3 3 | l. 223 E +0 | f $43 E \times 09$ |
| $1.006+02$ | $691 E+033833 \mathrm{E}+02$ | 7 deetco | $434 \mathrm{E}+01$ |  | $725 E+\infty 0$ | 375E-03 | 2 24E-02 | $830 \mathrm{E}+02$ |  |  |  |  | 3 30eke |  |  |
| $796 E+01$ | $696 E+003-475 E+02$ | $789 \mathrm{E}+02$ | $5396+01$ |  | -99E+00 | 301E-03 | $180 \mathrm{E}-02$ | $500 E+02$ | $2.46 E-03$ |  | 4 432E-0 | -1.14E-06 |  |  |  |
| $832 \mathrm{E}+01$ | $698 E+03-592 \mathrm{E}+02$ | 7.01E+62 | C 71E |  | $110 E+01$ | 2.37E-03 | 1.45E-02 | $397 \mathrm{E}+02$ |  | S E2E-09 |  | -1. | S0EE-02 | 1.16 |  |
| $502 \mathrm{E}+01$ | 704E+033 $7.760 \mathrm{E}+02$ | $780 \mathrm{E}+02$ | ${ }^{1} 726401$ |  | 1 ESEE01 | 232E-03 | $110 \mathrm{E}-02$ | $316 E+02$ | 1.37E-0. | 2.30E-03 | 4.35E- | . $712 \mathrm{EE-08}$ | S02t-02 | litee $0 \times 2$ | 2. $10 \mathrm{E}+\infty$ $3.21 \mathrm{E}+\infty$ |
| $3996+01$ | $704 \mathrm{E}+03 \mathrm{~S}-05 \mathrm{E}+02$ | 7 99E+02 | $103 \mathrm{E}+02$ |  | $184 \mathrm{E}+\mathrm{O}$ |  | $944 \mathrm{E}-03$ | $251 \mathrm{E}+02$ | 1.236 .03 | -1.70E-03 |  |  |  |  |  |
| $317 E+01$ | $709 \mathrm{ta3}$-1.11E+03 | $304 E+02$ | 1.265402 |  | $237 \mathrm{E}+01$ | $144 \mathrm{E}-03$ | $768 E-\infty$ | $190 \mathrm{E}+02$ | P 466 E-OS | -1. 2 SEE-03 | 4 4 75 E -0 | (7) OBE.08 |  | 20 | COE +02 |
|  | $715 E+03$-1 36E+03 | $811 \mathrm{E}+02$ | $155 \mathrm{E}+02$ |  | 3.03E+01 | 1.22E-03 | 6.23E-03 | $1586+02$ |  | + ME.O4 |  |  |  | S s 7 E | OLE +0, |
| $2006+01$ | $7.22 \mathrm{~F}+03 \mathrm{Ca}$-1.67E+03 | $819 E+02$ | $189 \mathrm{E}+02$ |  | $3.906+09$ | $1.04 \mathrm{E}-33$ | $807 E-03$ | $126 \mathrm{E}+02$ | 8 TEE-04 | ${ }_{-205}$ 200.04 | 4 SPE | - 5 SOE-08 | $788 E, 02$ $192 E-\infty$ | 887 | 02 |
| 1.59E+01 | $732 \mathrm{E}+03$-204E+03 | $830 E+02$ | $231 \mathrm{E}+02$ |  | 4 95E 01 | 86E.04 | 414 E -03 | 9 9eEror | 4 S4E-94 | - 266.04 |  |  |  |  |  |
| $1.266+01$ | $743 E+03-248 E+03$ | $843 \mathrm{E}+02$ | 282 E +02 |  | S 268 E01 | 7.53E-04 | 3 38E-03 | 7.93 E | 3 50e-04 | 2 SOE-O4 | ${ }_{4} 53$ | - 20E.08 | 1.00E-01 | 1.17E | -1 10E+03 |
| $100 \mathrm{E}+01$ | $759 \mathrm{E}+03-3$-22E+03 | 8 C0E402 | $343 E+02$ |  | 7.99E+01 | $844 E-24$ | 2.7E-. 3 | C 30E +01 | 2 ESE-04 | -1 80E-04 |  |  |  |  | -1.38E*03 |
| $798 E+\infty$ | $777 \mathrm{t}+033 \mathrm{~S}$ 57E+03 | $881 \mathrm{E}+02$ | $417 \mathrm{E}+02$ |  | $1.01 \mathrm{E}+02$ | 8496.04 | $227 \mathrm{E}-03$ | $800 \mathrm{E}+01$ | 2.296 .04 | -1 22E-04 | 4587 | - $428.0 \times 8$ | $1.206-01$ |  | -1.6IE +03 |
| $6322+00$ | 100E+03 -4 45E+03 | $907 \mathrm{E}+02$ | $505 \mathrm{E}+02$ |  | 1.27E 202 | 4 68E-94 | 1 18E-03 | $397 \mathrm{E}+\mathrm{O}$ | 1.ate-04 | 7 T 16-05 | 4 E2E- | -1.92E | 1 1seeor | ${ }^{1}$ | -1.02E 0103 |
| $502 \mathrm{E}+\infty$ | 0.28E+03 .5 38E+03 | $9.35 \mathrm{E}+02$ | $610 E+02$ |  | $1.59 \mathrm{E}+02$ | 4.00 E .04 | 1.53E.03 | $316 E$ | 1.47E-94 | - 15E.05 |  |  |  |  | -1 876.003 |
| $3986+00$ | 8 85E+03 +53E+03 | 9.81E+02 | $740 \mathrm{E}+02$ |  | 201E+02 | $342 \mathrm{E} \cdot 04$ | 1.26E-03 | 251 E 01 | 1.19E-04 | -1.3CE-0s | 4.7SE | -1.32E-07 | 1.7eeor | c.30E | -1.7EE+03 $-47 E+02$ |
| $317 \mathrm{E}+00$ | 9 10E+03 .7 C9E+03 | 1.03E+03 | 6 94E+02 |  | $252 \mathrm{E}+02$ | 2.22 E 04 | $1.04 \mathrm{E}^{-00}$ | 199E+01 | $275 E-05$ | -1.86E-08 | 4 POEE |  |  |  |  |
| $2.5225+00$ | $967 \mathrm{E}+03$ - 54E+03 | $190 E+03$ | $1.086+03$ |  | $3.16 E+02$ | $2.49 \mathrm{E}-04$ | C 52E-04 | 1 Sek-01 | - OSE-05 | 92EES | S00ECS | \% 46 | 2241009 | $1.025+04$ |  |
| $2.006+\infty$ | $104 \mathrm{E}+04$-1.15E+04 | $1.18 E+03$ | $130 E+03$ |  | 3.97E+02 | $2.15 E-04$ | $704 \mathrm{E}-\mathrm{O}$ | 1.26E+01 | 6 07E-8 | 1.36E-95 | 831 E - |  |  | 1.245 | $1.36 E+\infty$ $283 E+03$ |
| $1.59 \mathrm{E}+00$ | 1.13E+04 -1.36E+04 | $1.28 E+03$ | 1 56E+03 |  | 4.97E+02 | 1 18E-04 | 882E-04 | 98E+00 | 8 40E.05 | 1.SCE - 05 |  |  | 3 $177 \times$-9 | 1.44E 1004 | $283 E+\infty 3$ |
| $126 E+\infty$ $100 E+0$ |  | 1.41E ${ }^{\text {cos }}$ | 1 86E 03 |  | $835 \mathrm{E}+02$ | 1 134E-04 | $401 \mathrm{E}-04$ | 7.93E+00 | 4 SOE-08 | 1.71E-68 | 8 8 CeE.05 | 2.56E-05 | $317 E-91$ $385 E-01$ | 1.006cou |  |
| $1006+0$ | $138 \mathrm{E}+04.187 \mathrm{E}+0 \mathrm{4}$ | 1.56E+03 | $223 E+03$ |  | 780 E 402 | 1.39E-04 | 3996.0 |  | 396E-05 | 1 57E-08 | ¢ 20E-0s | 2.49E-98 | 3.005 .01 | 2.16ECO4 |  |
| 7966 | $155 \mathrm{E}+04.236 \mathrm{E}+04$ | $178 E+03$ | 2 67E+03 |  | $9 \mathrm{alE}+02$ | 1.21E-04 | $330 \mathrm{E}-0$ | $8005+\infty$ | 3 ExE-05 | 1.36E-05 | 7 26E.06 | 2.72E-06 |  |  |  |
| $632 \mathrm{E}-01$ | $177 E+04-2$ COE 04 | $201 \mathrm{E}+03$ | 3.18E+03 |  | $1.23 \mathrm{E}+\infty 3$ | 1.06E-04 | $2.74 \mathrm{E}-04$ | 3.97E $+\infty$ | 341 E .05 | 1 C6E-05 | A Sot-0 | $417 \mathrm{E}-08$ | 808 EPO | $27.47 \mathrm{E}+04$ |  |
| $502 \mathrm{E}, 01$ | $2028+0443$ 30E+04 | $228 \mathrm{E}+03$ | $374 E+03$ |  | $1.51 \mathrm{E}+03$ | 1296.05 | 2.30E-O4 | $318 E+\infty$ | 2 S0E-C5 | 1 48E.06 |  | 4BIE.08 | 8 63E-01 | ${ }_{2} 7151$ | 1.15ECO4 |
| 3 99E.01 | $238 E+044390 E+04$ | 2.70E+03 | $443 \mathrm{E}+03$ |  | 1.92E+03 | 2SE-05 | 1 D0E-O4 | $2.51 \mathrm{E}+\infty$ | 2 SEE-D | 1548 | 1 OSE-05 | S.15E-08 | $803 E-01$ 632001 | 271604 $206 E+04$ | 1.35E+04 |
| $317 \mathrm{E}-91$ $\mathbf{2} 52 \mathrm{E}-01$ | $276 E+04+595+04$ | 3.13E+03 | 6.21E+03 |  | 235 E -03 | $7206-\infty$ | 1 00E-O4 |  | 2 6SE-05 | 1.32E-05 | 1.34E-05 | COEED | $700 \mathrm{E}-01$ | 3015 | 1.71 CFECO4 |
| $2.52 \mathrm{E}-01$ | $3.21 E+04$-5 40E+04 | 3 4 E 203 | $812 \mathrm{E}+03$ |  | $2.06 E+03$ | 626E-05 | 1.34E-04 | 1.50E+00 | 2 250E-05 | $101 \mathrm{E}-6$ | 1 S8E-DS | C COE-06 | 7 POE.09 | $343 E+04$ | $140 \mathrm{CHO4}$ |
| $2006-01$ $150 E-1$ | $3.77 \mathrm{ta4} 528 \mathrm{E}+04$ | $428 \mathrm{E}+03$ | 7.12E603 |  | $350 \mathrm{E}+03$ | 8 56E.05 | 1936.04 | $126 \mathrm{E}+\infty$ | 2135.05 | $947 \mathrm{E}-06$ | 1 10et.0s | $753 \mathrm{E}-08$ | 082 EO | $302 \mathrm{LO4}$ | 1746 |
| 1268.01 |  | 808E+03 |  |  | $430 \mathrm{E}+03$ | 496E-S | 953E-08 | ${ }^{1896 E .01}$ | 1 93E-06 | O14E-6 | 1 95E-05 | 1166.08 | $1006+00$ | $421 E \times 04$ | 1 17E +04 |
| 1.00E-01 | 6.30 |  |  |  |  |  |  |  | 1 SJE | Cese-c | 231 E .05 | 100 E .05 | 112 ta | 447 E | $211 E+04$ |
|  |  |  |  |  |  |  |  |  |  | 93E-08 | 2 see |  | $1.268+\infty$ | $4706+04$ |  |




| $-257 E+00$ |
| :--- |
| $+2065 E-02$ |
| $+20 E-1.23 E-01$ |
| -3 |

$\begin{array}{ccc}+18 E+\infty 0 & 836 E .02 & 2.00 E E-01\end{array}$

$\begin{array}{llll}577 E+\infty & 2.015-02 & 876 E E-02 \\ 8.37 E+\infty & 155 E-0 & 403 E\end{array}$
$\begin{array}{ccc}8.37 E+00 & 1.01 E-02 & 855 E-02 \\ 113 E+01 & 132 E-02 & 403 E E 2 \\ 1 & 15 E-02\end{array}$

$\begin{array}{lll}1.48 E+01 & 1.12 E-02 & 252 E-02 \\ 1.28 E+01 & 8.91 E-03 & 211 E-02 \\ 210 E+01 & 18 E-03 & 180 E-02\end{array}$
$\begin{array}{lll}210 E+01 & 10 E-00 & 180 E-02 \\ 243 E+01 & 670 E-00 & 1.53 E-02\end{array}$








$\begin{array}{lll}216 E+02 & 547 E-04 & 1.4 E E-03 \\ 282 E+02 & 481 E-04 & 1.24 E-03\end{array}$

$380 E+02$ 3 20E.OA BEIE-OM




1.4E+00 $1.25 E 042$ 2 $44 \mathrm{E}-04$


41E+0 C.91E.N 1 OUE-04



$\begin{array}{llll}1.00 E+03 & 888 E+03 \\ 1 & 36 E+02 & 780 E+02 & -2.27 E+01 \\ 78 E+02 & -1 & 5 E E+01\end{array}$
 $\begin{array}{ccccc}532 \mathrm{E}+02 & 689 \mathrm{E}+03 & -656 \mathrm{E}+00 & 7.02 \mathrm{E}+02 & 7.44 \mathrm{E}-01 \\ 502 \mathrm{E}+02 & 890 \mathrm{E}+03 & -4.57 \mathrm{E}+01 & 782 \mathrm{E}+02 & 518 \mathrm{E}+00\end{array}$ $\begin{array}{llll}399 E+02 & 691 E+03 & -89 E+01 & 7.83 E+02 \\ 9 & 85 E+00\end{array}$ $317 \mathrm{E}+02892 \mathrm{E}+03-1.28 \mathrm{E}+02784 \mathrm{E}+02 \quad 1.45 \mathrm{E}+01$ $\begin{array}{llll}252 E+022 & 83 E+03 & -1.73 \mathrm{E}+02 & 786 \mathrm{E}+02 \\ 196 \mathrm{E}+01\end{array}$ $\begin{array}{llll}200 E+02 & 694 E+03 & -2 & 26 E+02 \\ 1 & 785+02 & 895 E+02 & 257 E+01\end{array}$
 $\begin{array}{llll}100 E+02 & 687 E+03-443 E+02 & 7 \text { P0EE+02 } & 4 \\ 7 & 03 E+01 \\ 7 & 02 E+01\end{array}$




 $\begin{array}{llll}252 E+01 & 719 E+03-157 E+03 & 15 E+02 & 1.78 E+02 \\ 200 E+01 & 72 E+03\end{array}$ $\begin{array}{llll}200 E+01 & 7.26 E+03 & -192 \mathrm{E}+03 & 824 \mathrm{E}+02 \\ 195 \mathrm{E}+01 & 217 \mathrm{E}+02\end{array}$ $\begin{array}{llllll}159 E+01 & 736 E+03 & -2 & 35 E+03 & 8.34 E+02 & 266 E+02 \\ 1.26 E+01 & 747 E+03 & -287 E+03 & 8 & 47 \mathrm{E}+02 & 3 \\ 1\end{array}$ \begin{tabular}{ccccc}
$100 E+01$ \& $7.61 E+03$ \& -2 \& $50 E+03$ \& 8 <br>
1 \& $62 E+02$ \& 3 \& $38 E+02$ <br>
\hline

 

$796 E+00$ \& $7.78 E+03$ \& $-42 E E+03$ \& $882 E+02$ <br>
\hline $8.85 E+02$
\end{tabular} $\begin{array}{lllll}0.32 E+00 & 7.09 E+03 & -23 E+03 & 0.06 E+02 & 5.03 E+02\end{array}$



 $\begin{array}{lllll}3.175 E+00 & 9.02 E+03 & -93 E+03 & 1.02 E+03 & 1.08 E+03 \\ 2.52 E+00 & 97 E+03 & -1.17 E+04 & 1.09 E+03 & 1.32 E+03\end{array}$ \begin{tabular}{lllll}
2.320 \& 200 \& $1.03 E+04$ \& $-1.17 E+04$ \& $1.09 E+03$ <br>
\hline \& $1.32 E+04$ \& $1.17 E+03$ \& $1.61 E+03$

 $1.59 \mathrm{E}+00112 \mathrm{E}+04-172 \mathrm{E}+04127 \mathrm{E}+03 \mathrm{i} 105 \mathrm{E}+03$ $\begin{array}{llll}1.26 E+00 & 1.24 \mathrm{E}+04 & -2.10 \mathrm{E}+04 & 1.40 \mathrm{E}+03 \\ 238 \mathrm{E}+03\end{array}$ $\begin{array}{lllll}1.00 E+00 & 1.39 E+04 & -2.55 E+04 & 1.50 E+03 & 2.89 E+03\end{array}$ $\begin{array}{llllll}7.08 E-01 & 1.58 E+04 & 3 & 07 E+04 & 1.79 E+03 & 3.48 E+03 \\ 6 & 32 E-01 & 182 E+04 & -3.68 E+04 & 207 E+03 & 4.18 E+03\end{array}$ 

$502 E-01$ \& $2.12 E+04$ \& -4 \& $43 E+04$ <br>
2 \& $207 E+03$ \& $4.18 E+03$ <br>
\hline

 $\begin{array}{llll}399 E-01 & 249 E+04 & -528 E+04 & 282 E+03 \\ 5 & 599 E+03\end{array}$ $317 E-012.99 E+04+26 E+043.39 E+03 \quad 7.12 E+03$ $252 \mathrm{E}-01363 \mathrm{E}+04-7.51 \mathrm{E}+044.11 \mathrm{E}+03 \quad 852 \mathrm{E}+03$ 

$2.00 E-01$ \& $4.26 E+04$ \& -8 <br>
\hline
\end{tabular} $\begin{array}{lllll}1.59 E-01 & 5.12 E+04 & -1 & 05 E+05 & 580 E+03 \\ 1.28 E-1 & 6.27 E+04 & -1.23 E+05 & 7.11 E+03 & 1.39 E+04 \\ & \end{array}$ $1.00 \mathrm{E}-017.53 \mathrm{E}+04-144 \mathrm{E}+05 \mathrm{~S}$ 8 $54 \mathrm{E}+03 \mathrm{l}$ With ET reagent
















$\begin{array}{cccccccc}155 E+02 & 3.40 E-04 & 161 E-03 & 307 E+01 \\ 1 & 1.32 E-03 & 316 E+01 & 2.21 E-04 & -2.46 E-05 & 635 E-06 & 619 E-07 \\ 1.92 E+02 & 234 E-04 & 1.08 E-03 & 251 E+04 & 1.91 E-04 & 252 E-05 & 7.01 E-00 & 2.02 E-07\end{array}$






| $101 E+03$ | $786 E-05$ | $265 E-04$ | $500 E+00$ | $889 E-05$ | $4.28 E-05$ | $1.78 E-05$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |


| $126 E+03$ | $76 E-05$ | $2.10 E-04$ | $507 E+00$ | $7.86 E-05$ | $4.11 E-05$ | $180 E-05$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $182 E+03$ | $582 E-05$ | $180 E-04$ |  |  |  |  |


|  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $204 E+03$ | $5.10 E-05$ | $180 E-04$ | $316 E+00$ | $7.21 E-05$ | $408 E-05$ | $228 E-05$ | $129 E-05$ |








$1.26 \mathrm{E}+03 \quad 7.01 \mathrm{E}+03 \quad 145 \mathrm{E}+02705 \mathrm{E}+02-164 \mathrm{E}+01$ $\begin{array}{llll}100 E+03 & 7.02 \mathrm{E}+03 & 7.17 \mathrm{E}+01 & 797 \mathrm{E}+02 \\ 7.06 \mathrm{E}+02 & 704 \mathrm{E} \\ 7 & 13 \mathrm{E}+00\end{array}$ | $1.82 E+02$ | $708 E+03$ | 0 |
| :---: | :---: | :---: | :---: | :---: |
| $6.32 E+00$ | $7.98 E+02$ | $-6.85 E-01$ |
| $57 E+01$ | $801 E+02$ | $9.72 \mathrm{E}+00$ | | $502 E+02$ | $7.08 \mathrm{E}+03-1.35 \mathrm{E}+02$ | $801 \mathrm{E} E+02$ |
| :--- | :--- | :--- | $\begin{array}{llll}3.99 E+02 & 7.10 \mathrm{E}+03-183 \mathrm{E}+02 & 8.05 \mathrm{E}+02 & 2.00 \mathrm{E}+01\end{array}$

 $\begin{array}{llll}2.52 \mathrm{E}+02 & 7.16 \mathrm{E}+03 & -2.06 \mathrm{E}+02 & \mathrm{~B} .12 \mathrm{E}+02 \\ 3.24 \mathrm{E}+01\end{array}$ $\begin{array}{llll}200 E+02 & 7.10 \mathrm{E}+03 & 3.40 \mathrm{E}+02 & 8.16 \mathrm{E}+02 \\ 159 \mathrm{E}+02 & 7.265 \mathrm{E}+01\end{array}$ $\begin{array}{lllll}1.59 \mathrm{E}+02 & 7.22 \mathrm{E}+03 & -4.04 \mathrm{E}+02 & 19 \mathrm{E}+02 & 4.58 \mathrm{E}+01 \\ 1.26 \mathrm{E}+02 & 7.25 \mathrm{E}+03 & -408 \mathrm{E}+02 & 82 \mathrm{E}+02 & 5.32 \mathrm{E}+01\end{array}$ \begin{tabular}{llll}
$1.00 \mathrm{E}+02$ \& $7.28 \mathrm{E}+03$ \& $-5.55 \mathrm{E}+02$ \& $22 \mathrm{E}+02$ <br>
Z \& $5.32 \mathrm{E}+01$ <br>
\hline

 $7.98 \mathrm{E}+017.32 \mathrm{E}+03$ - $88 \mathrm{E}+02$ a $30 \mathrm{E}+02 \quad 7.58 \mathrm{E}+01$ 

0 <br>
0 \& $32 E+01$ <br>
7 \& $37 E+03$ \& $-795 E+02$ \& $835 E+02$ <br>
\hline

 $5.02 \mathrm{E}+017.37 \mathrm{E}+03 \rightarrow 51 \mathrm{E}+02 \mathrm{Z}$.36E+02 $\quad 1.08 \mathrm{E}+02$ 

$3.99 E+01740 E+03-1.14 E+03$ <br>
$3.17 E+01$ \& $757 E+03$ <br>
\hline
\end{tabular}

 2.00E+01 7.78E+03 -1.97E+03 : $22 \mathrm{E}+02224 \mathrm{2} 2 \mathrm{E}+02$ 1.59E+01 7.03E+03 2 36E+03 a $90 \mathrm{E}+022.68 \mathrm{E}+02$ $1.28 \mathrm{E}+01: 10 \mathrm{E}+03-2.03 \mathrm{E}+03$ : $18 \mathrm{E}+02 \mathrm{~S}$ 3.21E+02



 $317 \mathrm{E}+001.03 \mathrm{E}+04+32 \mathrm{E}+03 \mathrm{I} 17 \mathrm{E}+03 \mathrm{O} 4 \mathrm{E} \mathrm{E}+02$ $\begin{array}{lllll}252 E+00 & 1.11 E+04 \\ 200 E+00 & 93 E+03 & 1.28 E+03 & 1.13 E+03\end{array}$


 7.08E-01 $1.00 \mathrm{E}+04.222 \mathrm{E}+042.15 \mathrm{E}+03 \quad 252 \mathrm{E}+03$ $02 E-012125 E+04-258 E+04244 E+03292 E+03$ 008-01 2.45E+04 -208E+04 $27 \mathrm{BE}+03 \quad 336 \mathrm{E}+03$


 .59E-01 5.20E+04 -5 45E+04 5.90E+03 . $18 \mathrm{E}+03$ $\begin{array}{llll}1.20 E-01 & 6.10 E+04 & 6.18 E+04 & 691 E+03 \\ 1.00 E-01 & 807 E+04 & \rightarrow 08 E+04 & 7.58 E+03 \\ 7 & & \end{array}$
$\begin{array}{ll}-353 E+\infty 0 & -1.25 \mathrm{E}-02 \\ -5 & -7.71 \mathrm{E} \cdot-02 \\ -212 \mathrm{E}\end{array}$
$\begin{array}{ccc}-2 \\ -212 E+00 & -3 & 00 E-02 \\ -1.15 E-01 \\ -121 E-01 & -1.151 E-01 & -106 E+00\end{array}$

| $-212+00$ |  |
| :---: | :---: |
| $-421 E-01$ | $-51 E-01$ |
| $180 E+\infty$ | $-1.06 E+00$ |

$\begin{array}{llll}188 E+\infty 0 & 1.92 \mathrm{E}-02 & 891 \mathrm{E}-02 \\ & 07 \mathrm{E}+00 & 183 \mathrm{E}\end{array}$
$\begin{array}{ccc}407 E+00 & 183 E-02 & 6.12 \mathrm{E}-02 \\ 677 \mathrm{E}+00 & 1.42 \mathrm{E}-02 & 435-02\end{array}$
$\begin{array}{lll}6 & 77 E+\infty & 1.42 E-02 \\ 981.35 E-02 \\ 981 E+00 & 1.24 E-02 & 3\end{array}$

| $1.34 E+01$ | $1.09 E-02$ | 3 |
| :--- | :--- | :--- |

$\begin{array}{lll}1.70 \mathrm{E}+01 & 5 S \mathrm{E}-03 & 2.17 \mathrm{E}-02 \\ 2.02\end{array}$
 $\begin{array}{ccc}2.35 E+01 & 6.94 E-03 & 1.57 E-02 \\ 2.74 E+01 & 882 E-03 & 14 E E O 2\end{array}$ $\begin{array}{cccc}2.74 \mathrm{E}+01 & 582 \mathrm{E}-03 & 134 \mathrm{E}-02 \\ 3.17 \mathrm{E}+01 & 480 \mathrm{E}-03 & 1.12 \mathrm{E}-02\end{array}$ $\begin{array}{ccc}3.17 E+01 & 460 E-03 & 1.12 E-02 \\ 368 E+01 & 380 E-03 & \text { STE-03 }\end{array}$ $\begin{array}{ccc:c}360 E+01 & 2 . M E-03 & S 1 E-03 \\ 5.05 E+01 & 262 E-03 & \text { SOE }\end{array}$



 | $0.33 E+01$ | $1.46 E-03$ | $383 E-03$ |
| :---: | :---: | :---: |
| $1.00 E+02$ | $22 E-03$ | $3.28 E-03$ | $\begin{array}{lll}1.10 E+02 & 1.02 E-03 & 3.28 E-03 \\ 1.74 E-03\end{array}$

 $\begin{array}{lll}1.71 E+02 & 7.12 E-04 & 1.01 E-03 \\ 200 E+02 & 809 E-04 & 1.50 E-03\end{array}$ $\begin{array}{ccc}2.08 E+02 & 6.99 E-04 & 1.50 \mathrm{E}-03 \\ 250 E+02 & 503 \mathrm{E}-9 & \end{array}$ \begin{tabular}{lll}
$304 E+02$ \& $502 \mathrm{EE-04}$ \& $1.3 \mathrm{EE}-03$ <br>
3 \& $4.2 \mathrm{E}-04$ \& $1.10 \mathrm{E}-03$ <br>
\hline

 

$3.74 E+02$ \& $3.63 E-04$ \& $1.10 E-03$ <br>
\hline
\end{tabular} $\begin{array}{ccc}462 E+02 & 312 E-04 & 700 E-04 \\ 566 E+02 & 209 E-04 & 83 E-04\end{array}$ $\begin{array}{lll}7.16 E+02 & 280 E-04 & 630 E-04 \\ 7.050 & 8.25 E-04\end{array}$ $\begin{array}{lll}876 E+02 & 207 E-04 & 8.25 E-04 \\ 1005-04\end{array}$

$\begin{array}{llll}1 & 00 E+03 & 1.83 E-04 & 300 E-04 \\ 1 & 35 E+03 & 166 E-04 & 00 E-04\end{array}$

| $133 E+03$ | $1.66 E-04$ | $3.08 E-04$ |
| :--- | :--- | :--- |
| 1 | $04 E+03$ | $1.46 E-04$ |
|  | $200 E-04$ |  |

$\begin{array}{lll}1 \text { OHE+03 } & 1.40 E-04 & 260 E-04 \\ 198 E+03 & 1.30 E-04 & 221 E-04\end{array}$
$243 E+03120 E-04 \quad 1.07 E-04$

| $200 E+03$ | $107 E-04$ | $1.00 E-04$ |
| :--- | :--- | :--- | :--- |



$\begin{array}{ccc}519 E+03 & 7.07 E-05 & 10 \mathrm{E}-08 \\ 011 \mathrm{E}+03 & 7.08 \mathrm{E}-05 & 10 \mathrm{E}-05\end{array}$










 $\begin{array}{llll}3 & 17 E+02 & 7.01 E+03 & -1.48 E+02 \\ 2 & 795 E & 502 & 1.68 E+01\end{array}$ $\begin{array}{llll}250 E+02 & 702 E+03 & -2.00 E+02 & 798 E+02 \\ 200 E & 288 E+01\end{array}$

 $\begin{array}{llll}100 E+02 & 700 E+03 & -5.23 E+02 & 803 E+02 \\ 796 E+01 & 593 E+01 \\ 710 E+008 & -296+02 & 808 E+02 & 73 E E+01\end{array}$

 $\begin{array}{ll}502 E+01 \\ 7.112 & 103-+95 E+02 \\ 3 & 007 E+02 \\ 1.13 E+02\end{array}$ | $390 E+01$ | $721 E+03$ | $-121 E+03$ | $112 E+02$ |
| :--- | :--- | :--- | :--- |
| $317 E+37 E+02$ |  |  |  |


 $150 E+01751 E+03-2$ 68E+03 $851 E+02301 \mathrm{E}+02$
 $\begin{array}{lllll}100 E+01 & 776 E+03 & -406 E+03 & 8 \\ 706 E+00 & 785 E+002 & 4.00 E+02\end{array}$
 $502 E+00$ a $41 E+03-7.36 E+03$ O $33 E+028: 35 E+02$


 $\begin{array}{llllll}159 E++00 & 1.16 E+04 & -2.06 E+04 & 1.20 E+03 & 193 E+03 \\ 131 E+03 & 2.30 E+03\end{array}$ 1.26E+00 1.28E+04-2.57E+04 1.45E+03 $202 \mathrm{EF}+03$
 7.00E-01 $1.67 \mathrm{E}+04-3.77 \mathrm{E}+041.80 \mathrm{E}+03 \quad 4.28 \mathrm{E}+03$

 3.17E-01 $3.32 \mathrm{E}+04 \mathrm{~F} 786 \mathrm{E}+043 \mathrm{3} 7 \mathrm{E}+03891 \mathrm{E}+03$ $252 E-014.02 E+04-9.22 E+04455 E+03105 E+04$

 | $1.59 E-01$ | $7.07 E+04$ | $-1.28 E+06$ | $801 E+03$ |
| :---: | :---: | :---: | :---: |
| $1.43 E+04$ |  |  |  |
|  | $28 E-01$ |  |  |
| 7 | $48 E+04$ | -1 | $58 E+08$ |
|  | $48 E+03$ | $1.79 E+04$ |  |

 Win ET magonk

 OOE +037 TOME 1303 I $33 E+02797 E+02-151 E+01$ (32E+02 7.00E+03 +. $77 E+01803 E+02995 E+\infty$ $302 \mathrm{E}+02$ 7.10E +03 -1.45E+02 8 O5E +02 1.64E+01 $\begin{array}{llll}399 E+02 & 7.13 E+03-200 E+02 & 808 E+02 & 2.27 E+01\end{array}$ $\begin{array}{llll}3.17 E+02 & 7.16 E+03 \\ 252 E+2.57 E+02 & 8 & 12 E+02 & 291 E+01\end{array}$ $\begin{array}{llll}2.52 E+02 & 7.19 E+03 \\ 200 E+02 & 3.16 E+02 & 16 E+02 & 3.58 E+01\end{array}$ $\begin{array}{lllll}1.50 E+02 & 7.25 E+03 & -402 E+02 & 19 E+02 & 433 E+01 \\ 1502 & 23 E+02 & 509 E+01\end{array}$
 1.00E+02 7.34E+03 - $33 E+02: 32 E+02 \quad$ 7.17E+01














 $150 \mathrm{E}+\infty 01.50 \mathrm{E}+04-1.00 \mathrm{E}+04181 \mathrm{E}+03 \mathrm{~S} 1.24 \mathrm{E}+03$ $1.28 \mathrm{E}+001.7 \mathrm{E}+04-1.20 \mathrm{E}+04200 \mathrm{E}+031.36 \mathrm{~S}+03$ . $006+001.94 E+04-1.20 \mathrm{E}+04 \mathrm{Z} 2.20 \mathrm{E}+031.47 \mathrm{E}+03$ 7 98E-01 $2.11 E+04-1.40 E+042.40 E+03 \quad 1.50 E+03$ | 3 | $32 E-01$ | $233 E+04$ | $-1.52 E+04$ |
| :--- | :--- | :--- | :--- |
| $02 E-01$ | $2.53 E+04$ | $-1 ., 1 E+04$ | $206 E+03$ |
| $1.72 E+03$ |  |  |  |
| $1.83 E+03$ |  |  |  |

 $317 E-012$ ege +04 -1 01E+04 3 3.30E +03 $216 E+03$ 2.52E-01 3.20E 04 -2.03E+04 3 O3E +03 2.30E+03

 1.00E-01 4.40E+04 -271E+O4








 $1.0 E 61$






















 $\begin{array}{ccc}-468 E+00 & -4.19 E-03 & -260 E-02 \\ -469 E+00 & -7.26 E-03 & -386 E-02\end{array}$ $\begin{array}{ccc}-125 E+\infty & -7.26 E-03 & -386 E-02 \\ -32 E+\infty 0 \\ -1.30 E-02 & +34 E-22\end{array}$

 $\begin{array}{llll}240 E-01 & 1.65 E-01 & 7.08 E-01 \\ 2.38 E+00 & 2.20 E-02 & 51 E-02\end{array}$ $\begin{array}{ccc}2.38 E+00 & 2.28 E-02 & 181 E-02 \\ 400 E+00 & 107 E-02 & 5.00 E-02\end{array}$ $\begin{array}{lll}4.0 E+\infty & 1.07 E-02 & 8.00 E-02 \\ 7.07 E+00 & 1.36 E-02 & 3.03 E-02\end{array}$ $\begin{array}{lll}1.87 E+00 & 1.36 E-02 & \text { J.08E-02 } \\ 1.12 E+01 & 1.15 E-02 & 208 E-02\end{array}$ $\begin{array}{llll}1.51 E+01 & 1.00 E-02 & 237 E-02 \\ 1.80 E\end{array}$ $\begin{array}{lll}188 E+01 & 837 E-03 & 195 E-02 \\ 2.26 E+01 & 728 E-00 & 15 E-0\end{array}$ $\begin{array}{llll}2.26 E+01 & 7.28 E-08 & 18 E E-02 \\ 200 E+01 & 18 E-03 & 1.3 B E-02\end{array}$ $\begin{array}{lll}26 E+01 & 18 E-03 & 1.38 E-02 \\ 317 E+01 & 8.16 E-09 & 1.17 E-02\end{array}$ | $3.71 E+01$ | $4.24 E-00$ | $1.17 E-02$ |
| :--- | :--- | :--- |
| $82 E-03$ |  |  |




 $\begin{array}{llll}100 E+0 & 1.13 E-03 & 400 E-\infty \\ 100 E+02 & 14 B E-\infty & 3 & 32 E-\infty 3\end{array}$

 $\begin{array}{llll}1.01 E+\infty 2 & \text { E.10E } & \text { On } & 1.00 \mathrm{E}-03 \\ 2.36 E+02 & 100 E-04 & 100 \mathrm{E}\end{array}$

 $452 E+\infty 2881 E-04$ O $82 E-04$ $500 E+02807 E-04800 E-04$

 $\begin{array}{llll}1.20 E+00 & 308 E-04 & 4 . & 13 E-04 \\ 1.40 E+00 & 3.40 E-04 & 3 & 57 E-04\end{array}$

 $\begin{array}{lll}2.06 E+05 & 271 E-04 & 2.41 E-04 \\ 235 E+05 & 240 E-04 & 210 E-04\end{array}$ $\begin{array}{lll}235 E+03 & 248 E-O 4 & 2.10 E-01 \\ 250 E+03 & 2.27 E-04 & 100 E-04\end{array}$ $203 E+03$ 2.13E-04 1.73E-04

 $4.16 E+03$ I.ESE-04 $1.14 E-0$






Irequency $2 \quad \mathrm{Zn}^{\text {n }} \quad \mathrm{Z} / \mathrm{cm}^{2} \mathrm{Zn}^{\prime \prime} \mathrm{cm}^{2}$
 $126 E+03887 E+03 \quad 188 E+02 \quad 779 E+02-213 E+0$

 $502 \mathrm{E}+02689 \mathrm{E}+03-233 \mathrm{E}+01781 \mathrm{E}+02 \quad 264 \mathrm{E}+00$ $399 E+02690 \mathrm{E}+03-0.32 \mathrm{E}+017.72 \mathrm{E}+02 \quad 044 \mathrm{E}+00$
 $200 \mathrm{E}+02693 \mathrm{E}+03-287 \mathrm{E}+02736 \mathrm{E}+022 \mathrm{3} 25 \mathrm{E}+0$ 1.59E+02 $694 \mathrm{E}+03-368 \mathrm{E}+027$ 87E+02 $417 \mathrm{E}+01$ $128 \mathrm{E}+02696 \mathrm{E}+03-468 \mathrm{E}+027 \mathrm{79E}+02 \mathrm{5} 29 \mathrm{E}+01$


 3 99E $+01713 \mathrm{E}+03-1.36 \mathrm{E}+03800 \mathrm{E} \mathbf{E}+02 \quad 1.54 \mathrm{E}+02$

 $1.59 \mathrm{E}+01745 \mathrm{E}+03$. $-08 \mathrm{E}+03 \mathrm{~B} 44 \mathrm{E}+0222 \mathrm{ISE+02}$ 1.28E+09 7.58E+03 -3 78E+03 $859 \mathrm{E}+022$
 $796 \mathrm{E}+007$ 92E+03 -5.71E+03 $898 \mathrm{E}+02 \quad 647 \mathrm{E}+02$ $32 \mathrm{E}+00817 \mathrm{E}+03 \quad-702 \mathrm{E}+03926 \mathrm{E}+02796 \mathrm{E}+02$
 3. $17 \mathrm{E}+00946 \mathrm{E}+03$-1,30E+04 $1.07 \mathrm{E}+03$ 1. $47 \mathrm{E}+03$ $2.52 \mathrm{E}+00102 \mathrm{E}+04$-1 $60 \mathrm{E}+041.16 \mathrm{E}+03 \mathrm{1} 31 \mathrm{E}+03$ $200 \mathrm{E}+00111 \mathrm{E}+04-195 \mathrm{E}+041.28 \mathrm{E}+03 \quad 2.21 \mathrm{E}+03$ $159 \mathrm{E}+001.24 \mathrm{E}+04-237 \mathrm{E}+04140 \mathrm{E}+03 \quad 269 \mathrm{E}+03$ $\begin{array}{lllll}1.26 E+00 & 149 \mathrm{E}+04 & -291 \mathrm{E}+04 & 169 \mathrm{E}+03 & 330 \mathrm{E}+03 \\ 100 \mathrm{E}+00 & 189 \mathrm{E}+04 & -360 \mathrm{E}+04 & 192 \mathrm{E}+03 & 408 \mathrm{E}\end{array}$ $\begin{array}{lllll}100 E+00 & 189 E+04 & -3.30 E+04 & 1.02 E+03 & 4.08 E+03\end{array}$ $632 \mathrm{E}-01220 \mathrm{E}+04-5.10 \mathrm{E}+0442.50 \mathrm{E}+03 \mathrm{~S} \quad \mathrm{~s} .70 \mathrm{E}+03$ S.02E-01 $281 E+04$ - $43 E+04296 E+03605 E+03$ 399E-01 3 15E+04 $-7.36 E+04 ~ 350 E+03$ : 35E+03 $317 E-01385 \mathrm{E}+04$ - $869 \mathrm{E}+044.37 \mathrm{E}+03$ O $85 \mathrm{E}+03$
 $159 E-01895 E+04-14 \mathrm{AE+05} 788 \mathrm{E}+03 \mathrm{l}$ $1.28 E-01$ B $52 E+04-1.70 E+05968 E+03 \quad 1.82 E+04$ 1.00E-01 $1.04 \mathrm{E}+05 \quad-2.01 \mathrm{E}+05 \quad 1.17 \mathrm{E}+04 \quad 227 \mathrm{E}+0$ With ET roagert

| ZRs |  |  |  | $r$ | r" | rim | r/m | 1/sart(w) |  | 4/ac(s) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $-240 E+\infty$ |  | -2 41E-02 | $1.28 \mathrm{E}+04$ | $275 E-03$ |  |  | -2 68E-07 |  |  |  |
| 30 | 48E-3 | -3 27E-02 | 988 | 43 E |  |  | -11E.07 | OOE- | -6 21E | $\rightarrow$ SOE |
| 19 | $23 \mathrm{E}-3$ | $-458 \mathrm{E} \cdot 02$ |  | -12E | 24 | 11 | -302E | 112 E | -1 319 |  |
| 1.47 | 7.796 | -7.25E |  |  |  |  |  | 1.28 E -02 | -2 11 |  |
| -. 10 | 200 E | -1 47E-01 | 5 DOE 03 | 1 22E-01 | $422 \mathrm{E}-1$ | 243 C | 044 | 1.41E.02 | 130 |  |
| 536 |  | 231 | 3 97E+03 | - 30E-02 | 346 | 236 E | © 70E-05 | $1.596-02$ |  |  |
| 3 37E- | 4 75E-0 | 3 72E-0 | 3 18E+ | - 222 | 3.13 | -7 02 | -93E-05 | 1.78 E | 22 |  |
| $138 \mathrm{E}+0$ | $149 \mathrm{E}-02$ | 1.04E | $251 \mathrm{E}+03$ | 135 | - 50E- | 5.39 | -2 22 E | $200 \mathrm{E}-2$ |  | 15 |
| 33E + + | 141E-03 | 5.04E-02 | 1 100E+03 | 3 85E | 313 | 183 | -1.57E-05 | $2.24 \mathrm{E}-02$ |  |  |
| $368 \mathrm{E}+0$ | 804E-03 | 4 02E-02 | $1.58 \mathrm{E}+03$ | 382 | -1 83E-02 | 229 | -1.16E.05 | $2.51 \mathrm{E}-02$ | 10 |  |
| $508 \mathrm{E}+0$ | 4 caE-03 | 3 O0E-02 | 1.28E+03 | 345 E | -1.21E-02 | 274 |  | $282 \mathrm{E}-02$ |  |  |
| TE+00 | $384 \mathrm{E}-03$ | 2 34E-02 | 9 98E+02 | 31 | +66E-03 | 3.14E | + 67E-08 | $317 \mathrm{E}-02$ | 3.7 | 1.02 |
| 42E+00 | 2 94E-03 | 1.84E-02 | $793 \mathrm{E}+02$ | 2 68E | d | 3.37E | -7 62E-00 | $355 E-02$ | 13 |  |
| 1.11E+01 | 2 45E-03 | 1.47 | 630 E | 2 23E | $420 \mathrm{E}-0$ |  | - 80 | 96E-02 |  |  |
| +19 | 1 08E-03 | 1.18E-02 | $500 \mathrm{E}+02$ | 100 | 3.08 | 380 | -12E-0 | $447 \mathrm{E}-02$ |  |  |
| 4 E | 1 62E-03 | - 50E-0 | 3 07E+02 | 163 E | 2.19E-03 |  | - $51 \mathrm{E}-0$ | $502 \mathrm{E}-02$ | 21 | $294 \mathrm{CHO2}$ |
| $243 \mathrm{E}+01$ | 1 62E-03 | 800 | $318 E+02$ | - 79E-C | $201 E-03$ | 2.70 | + 30 | 5 63E.02 | $1{ }^{1} 3 \mathrm{E}$ | 4.18E+02 |
| $280 \mathrm{E}+01$ | 1.14E-03 | 6 27E | 251 | 116 | 1.12E-03 | 404 | 4 45E-0 | $632 \mathrm{E}-02$ | 4 | 4 |
| $49 \mathrm{E}+01$ | -42E-04 | 5.11E-03 | 1.99E+02 | 101 E | 7.02E-0 |  | -1 | $709 \mathrm{E}-02$ | 01 | - 79E*02 |
| $429 \mathrm{E}+01$ | 7.72E-04 | 4 17E-03 | $1.58 \mathrm{E}+02$ | 192 E | . $585 \mathrm{E}-04$ | 58 | -3 SIE-C0 | 7 0SE-02 | B7E | 03E-02 |
| 525 E | 6.25E-04 | 3 39E-03 | 1.28E+02 | ${ }^{0}$ | 382 E -0 | 638 | 2 88E-06 |  | 10 | 67E+02 |
| $641 \mathrm{E}+01$ | $508 E-04$ | 2.77E-03 | - $08 \mathrm{E}+01$ | 724 E | 2.3 | 7.2 | -2 40E-0 | $1006-01$ |  |  |
| 7.83E+01 | 4.12E | 2.26E-03 | 3E40 | 6 61E | 1.52E-0 | 13 | -1 11 E | 1.12E-01 | 1 4AE | 30E+02 |
| 32E+01 | $333 \mathrm{E}-04$ | 1.84 E - | 30 | 800 E | 85E-05 | - | -1 30E-0 | $1.26 \mathrm{E}-01$ | 181 | 2 20E+02 |
| 17E+02 | $272 \mathrm{E}-04$ | 1.50E-03 | 5 OOE+OI | 58 | 40 | 1.13 | - O1E-0) | $141 \mathrm{E}-01$ | 1.78 | $124 E+02$ |
| 4E+02 | $2.22 \mathrm{E}-04$ |  | 307 E 01 | \$ 34E- | 7.00 | 1.3 | 1.78E-07 | 1 S0E-01 | $187 \mathrm{E}+03$ |  |
| $1.61 \mathrm{E}+02$ | 1.03 | 988 | 16E+01 | $507 \mathrm{E}-6$ | 1.63E-05 | $161 \mathrm{E}-\mathrm{O}$ | 8.15E-07 | 1.78 E | 107 | 1 |
| $228 \mathrm{E}+02$ | 1.53E-04 | $804 E-0$ | $2.51 \mathrm{E}+09$ | 4 ase-a | $2.99 E-05$ | 1.03E-0 | 1.10E-06 | $200 \mathrm{E}-01$ | $205 \mathrm{e}+03$ | 1.27E 022 |
| $291 \mathrm{E}+02$ | 1.29E-04 | 853 E -4 | $1.99 \mathrm{E}+01$ | 4 B5E-0 | $4.60 \mathrm{E}-0$ | 234 E | 231 EPO | $224 \mathrm{E}-0$ | 2.13E+03 | . 21 |
| 3.75E+02 | 1.10E-04 | 8.30E | $1.58 \mathrm{E}+01$ | 447E-04 | 881E-05 | 2 83E-0s | 3 S5E-0 | $251 \mathrm{E}-01$ | 22 |  |
| $82 \mathrm{E}+02$ | - 42E-03 | 432 E | 1.28E+01 | $4316-04$ | 36E-0S | 3.43E-05 | 8.00E-00 | $282 \mathrm{E}-01$ | $227 E+03$ | 3 S |
| 6.22E+02 | - 16E-03 | 3 53E-04 | ${ }^{\text {P 08E }}$ - ${ }^{\text {co }}$ | 417 E | 7135 | $418 \mathrm{E}-05$ | 7.15E-00 | 3.17E-01 | $233 \mathrm{E}+03$ | 3 00E +02 |
| O9E+02 | 7.78E-03 | 282 E | 7 93E-00 | 3 28E-04 | -20E-05 | 5 OOE-O5 | 1.03E-03 | 3 SSE-0 | $242 \mathrm{E}+03$ | 8 OIE 02 |
| 4E+03 | ( 36 E | 227 E | 30E+00 | 3 s6E-04 | $804 \mathrm{E}-05$ | ¢ 12E-05 | 1.44E-05 | $196 E-01$ | 246 |  |
| 36E+03 | 5 42E-05 | 192 E | $500 \mathrm{E}+00$ | 3 73E-00 |  | 7.46E-05 | 1.78E.05 | 4 47E-01 | 2 SLE+0S | O4E |
| 71E+03 | 4.71E-05 | 159 E | 3 07E+00 | 3 S3E-04 | 6 86E-09 | B9E-05 | $226 \mathrm{E}-05$ | 802 E -01 | $260 \mathrm{E}+03$ | 析 |
| $18 \mathrm{E}+03$ | $411 \mathrm{E}-05$ |  | 3 16E+00 | 3 39E-04 | , 52E-05 | $107 E-04$ | $301 \mathrm{E-05}$ | 8 e3E-01 | $274 \mathrm{Et03}$ |  |
| 2 BOE +03 | $361 \mathrm{E}-05$ | 1.08 E | 2 S1E+00 |  | 870 -05 | 1 28E-0a | 3 87E-0S | - 32E-01 | 2 ceet03 | CuE |
|  | 3 26E-05 | 1.96E-05 | $1.99 \mathrm{E}+00$ | 3 OSE-04 | S PSE-05 | 1.53E-0 | 4 OME.-0S | $700 \mathrm{E}-01$ | $2 \mathrm{l7E} 5$ | 64E |
| $52 \mathrm{E}+03$ | 2 ESE-0S | 7.41E-05 | 1.58E +00 | 2 00E-04 | \% 00E-05 | 1 13E-04 | 67E-05 | 7.95E-01 | 3 11E-03 | .03 |
| 72E+03 | 2 52E-03 | 6.14E-05 |  | $268 \mathrm{E}-04$ | - S0E-05 | 2 13E-a | 7.56E-03 | C02E-01 | 3 31E-03 |  |
| 10E+03 | $2.23 \mathrm{E}-05$ | 8.14E-05 | - 80E-01 | 2 47E-04 | - 29E-05 | $247 \mathrm{E}-0$ | 306.05 | -02E-0 | 3 SSE+03 |  |
| bE+03 | $198 \mathrm{E}-05$ | $429 \mathrm{E}-05$ |  | $227 \mathrm{E}-04$ | O 41E-05 |  |  |  |  |  |
| $1.10 \mathrm{E}+04$ |  |  |  |  |  |  |  |  |  |  |

 $\begin{array}{llll}1.59 E+03 & 703 E+03 & 210 \mathrm{E}+02 & 797 \mathrm{E}+02 \\ 126 \mathrm{E}+03 & 704 \mathrm{E}+01 \\ 1 & 1.21 \mathrm{E}+02 \\ 790 \mathrm{E}+02 & -137 \mathrm{E}+01\end{array}$


 $302 \mathrm{E}+02712 \mathrm{E}+03-1.27 \mathrm{E}+02: 107 \mathrm{E}+02 \mathrm{i} 14 \mathrm{E}+01$ $309 \mathrm{E}+027.15 \mathrm{E}+03-105 \mathrm{E}+02: 10 \mathrm{E}+02 \quad 2.22 \mathrm{E}+01$ $3.17 \mathrm{E}+027.18 \mathrm{E}+03-2.65 \mathrm{E}+02: 14 \mathrm{E}+02 \mathrm{BOOE}+01$
 $\begin{array}{ccccc}2.00 \mathrm{E}+02 & 7.23 \mathrm{E}+03 & -4.09 \mathrm{E}+02 & 0.22 \mathrm{E}+02 & 463 \mathrm{E}+01 \\ 1.59 \mathrm{E}+02 & 7.29 \mathrm{E}+03 & +93 \mathrm{E}+02 & \mathrm{El} 27 \mathrm{E}+02 & 8.59 \mathrm{E}+01\end{array}$

 7.06E+01 $744 \mathrm{E}+03+44 \mathrm{E}+02 \mathrm{E} .44 \mathrm{E}+02 \quad 3.57 \mathrm{E}+01$ .32E+01 7.51E+03-1.01E+03 8. $52 \mathrm{E}+02 \mathrm{I}$ 1.14E+02 $\begin{array}{llll}102 E+01 & 750 E+03 & -1.25 E+03 & 60 E+02 \\ 1.42 E+02\end{array}$


 $\begin{array}{lllll}200 E+01 & \text { B. } 19 E+03 & 2 & 3 E E+03 & \text { D.28E+02 } \\ 2.70 E+02\end{array}$ 4.59E+01 44E+03 $282 \mathrm{E}+03$ - $57 \mathrm{E}+02 \mathrm{Z}$ 20E+02 1.28E+01 $878 E+03$. $3.32 E+03993 E+0223.77 E+02$ . $00 \mathrm{E}+019$ 16E+03 3 POE 0 O3 1 OME+03 $442 E+02$ | $7.86 E+00$ | $88 E+03$ | 4 | $53 E+03$ | $1.10 E+03$ |
| :---: | :---: | :---: | :---: | :---: |
| 3 | 5 | $5.16 E+00$ | $103 E+04$ | -5 |

 3.99E+00 $1.22 E+04+67 E+03$ 1.36E+03 $756 E+02$ $317 \mathrm{E}+00$ 1.33E+04 $-7.32 \mathrm{E}+03$ 1.51E+03 $\quad 31 \mathrm{E}+02$ $252 \mathrm{E}+001.46 \mathrm{E}+04,-7,00 \mathrm{E}+031$ 105E+03 $806 \mathrm{E}+02$ $200 \mathrm{E}+\infty 01.50 \mathrm{E}+04+38 \mathrm{E}+03181 \mathrm{E}+03$ O $50 \mathrm{E}+02$
 $\begin{array}{lllll}1.26 E+00 & 188 E+04 & +890 E+03 & 2.13 E+03 & 1.02 E+03 \\ 1.00 E+00 & 201 E+04 & 28 E+03 & 220 E+03 & 105 E+03\end{array}$ 7 06E-01 $215 \mathrm{E}+04-4 \mathrm{~A} E+03243 \mathrm{E}+03 \mathrm{~S}$ $632 E-012.30 E+04-980 E+032.60 E+03 \quad$ T.12E+03 $502 E-01242 E+04-102 E+04275 E+03116 E+03$ $390 \mathrm{E}-01257 \mathrm{E}+04 \cdot 1.07 \mathrm{E}+04291 \mathrm{E}+03 \mathrm{~T} 21 \mathrm{E}+03$ $317 E-01270 E+04-111 E+04300 E+03$ I $26 E+03$

 $126 \mathrm{E}-01344 \mathrm{E}+04-151 \mathrm{E}+043$ 30E $+03,172 \mathrm{E}+03$ $1.00 \mathrm{E}-013$ 04E+04 -1.70E+04 $413 \mathrm{E}+03$ 1.02E+03

 $260 E+00$-1 $34 E-02$-7.05E-02 $-100 E+00-458 E-02-201 E-01$ .18E+00 $1.02 \mathrm{E}-012.75 \mathrm{E}-01$ $\begin{array}{llll}1.71 E+00 & \text { C 4PE-02 } & 1 \text { ISE-01 }\end{array}$ 46E 400 1.63E-02 $382 \mathrm{E}-02$ 1.20E+01 1.21E-02 2.41E-02 1.70E+01 $0.66 E-03$ 2.18E-02 2.10E+01 $1.13 \mathrm{E}-03$ P. $7 \mathrm{7DE}-02$ $257 E+09678 E-031.48 E-02$ \begin{tabular}{lll}
$3.03 E+01$ \& $561 E-03$ \& $1.24 E-02$ <br>
\hline $61 E+01$ \& CSBE <br>
\hline

 $4.20 \mathrm{E}+01388 \mathrm{E}-03 \mathrm{E}$ ETZE-03 $507 \mathrm{E}+01$ 3.24E-03 7.91E-03 83E+01 2 SOE-03 8.00E-03 $22 E+012.30 E-03$ S. 1 EE-03 .70E+01 $1.06 E-034$ I2FE-03 

$1.05 E+02$ \& $1.06 E-03$ \& $3.02 E-03$ <br>
\& $27 E+02$ \& $143 E-03$ <br>
\hline
\end{tabular} $\begin{array}{lll}1.56 E+02 & 1.23 E-03 & 2.53 E-03\end{array}$ $1.02 \mathrm{E}+02 \mathrm{I} \quad 107 \mathrm{E}-03 \mathrm{Z} 2.11 \mathrm{E}-03$ 37E002 0 42E-04 $1.78 E-09$ 2.07E 022 O S8E-04 P.40E-03 $3.72 \mathrm{E}+0227.56 \mathrm{E}-04 \mathrm{I} 1.21 \mathrm{E}-03$ TSE+02 SDOE-04 1.00E-03 T.OEE+02 S.WE-O4 8 POE-OU 52E-02 B.57E-04 8 sece-04 O1EP03 \$25E-04 4 COE-OA 1 16E-03 4 POE-04 $424 E-0$ I3E+03 4 TUE-O4 3 OAE-O $183 E+03$ 4. $27 E-04$ I 1 SE-O 1 BOE +03 4OOE-OA 2 LEE-O $106 \mathrm{E}+033$ 30E-04 2.26E-0 $211 E+03337 E \cdot 04205 E-0$ $228 E+03$ 3 30E-04 1 EBE-OL $24 \mathrm{E}+03 \mathrm{~B} .18 \mathrm{E}-04 \mathrm{~T}$ 1.70E-0 2 6SER03 $203 E-04$ I.56E-0 $\begin{array}{ll}260 E+03 \\ 10 E+03 & 2.47 E-04 \\ 1.37 E-O\end{array}$

3 $33 \mathrm{E}+03 \mathrm{Z}$ 25E-04 130 EA






| quency | Z | Z" | 2/cm ${ }^{2}$ | 2"/cm ${ }^{2}$ | R. | 2-Rs | $r$ | ${ }^{\mathbf{r}}$ |  | $r$ |  | Y/o | YMo |  |  | 1/me(s) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $200 \mathrm{E}+03$ | $886 E+03$ |  | $778 \mathrm{E}+02$ |  |  | $-242 E+00$ | -1.50E-03 | 2 49E-02 | $1.28 \mathrm{E}+04$ | $-2 \text { S4E-03 }$ |  |  | 7 | ) | 1.44E 002 |  |
| $159 \mathrm{E}+0$ | $6^{88 \mathrm{E}+0}$ | 257 | $778 \mathrm{E}+$ | -292E+01 |  | $-224 E+00$ | $261 E-03$ | $941 \mathrm{E}-02$ | $098 E+03$ | $-545 E-03$ | - ScE-03 |  |  |  |  | 1 BuEs02 |
| $128 \mathrm{E}+03$ | 887 E | $175 \mathrm{E}+02$ | 7.79E+ | -1.98E+01 |  | $-180 \mathrm{E}+00$ | - $28 \mathrm{EE}-03$ | S $01 E-02$ | 7 93E-03 | -1 3EE-02 | - $304 \mathrm{E}-02$ | -1 69E | -3 83E-06 | 1.12E-02 | -1.21E+01 |  |
| $1006+03$ | $687 \mathrm{E}+03$ | $103 \mathrm{E}+02$ | 779 | -1.17E |  | -1 19E+00 | -64E-0 | - $47 \mathrm{E}-02$ | C $30 \mathrm{E}+0$ | -7 71E-02 | -2 29 E -0 | -1.22E-0 | - 4 28E-05 | 1.2EE-02 | - $\rightarrow$ - 57 E -01 | $276 E+0$ $-34 E+\infty$ |
| $796 \mathrm{E}+02$ | $688 E+03$ | $300 \mathrm{E}+$ | 780 E | -42E+00 |  | -5 S0E-01 | -292E-02 | 2 22E-01 | 8 00E+03 | 7 63E-02 | 9 83E-01 | ${ }^{1}$ |  | 141E-02 |  |  |
| 6.32E+02 | $088 \mathrm{E}+03$ | $-168 \mathrm{E}+0$ | 7.00E+02 | 1.91E-01 |  | -6.12E-02 | -1.88E+0 | $43 \mathrm{4E+00}$ | $397 \mathrm{E}+03$ | 1.01E+00 | - $-43 E+00$ | 1 S2E-05 | 7 S | $141 E-02$ $199 E-02$ | 3 $018-01$ | $281 E+00$ $102 E-01$ |
| $502 \mathrm{E}+02$ | 6.89E+0 | - 25E+01 | 7 82E+02 | $7.09 \mathrm{E}+00$ |  | $1.12 \mathrm{E}+\infty 0$ | $218 \mathrm{E}-02$ | 1.38E-01 | 316 E | -474E-03 | - 46 |  |  | $1{ }^{1} \mathrm{TEE-02}$ | - $28 E-01$ |  |
| 3 99E+02 | 6 90E+03 | -1.26E+02 | 7.83E+02 | $143 E+01$ |  | $219 E+00$ | $104 \mathrm{E}-02$ | 6 BIE-0 | $2.51 \mathrm{E}+03$ | $204 E-03$ | - $74 \mathrm{E}-02$ | 0.13 | 1.40E-05 | $200 E-02$ | $145 E$ | $2 \mathrm{CrEx}+1$ |
| $3.17 \mathrm{E}+02$ | $691 \mathrm{E}+03$ | -1.92E+02 | 7.84E+02 | 217 E 01 |  | 3.39E+ | 7.00E-03 | 4 4EE-02 | $199 E+03$ | 2 08E-03 | -2 14E-02 | 1.49E- | -1 07E-05 | $224 \mathrm{E}-02$ | 6.3SE |  |
| $252 \mathrm{E}+02$ | $892 \mathrm{E}+03$ | $-282 \mathrm{E}+02$ | 7.85E+02 | 2 98E+01 |  | $472 \mathrm{E}+6$ | 5.19E-03 | $328 E-02$ | $1.58 \mathrm{E}+03$ | $300 E-03$ | -1.40E-02 | 1 OOE | + BEE-08 | 2 S1E-02 | $145 E$ | - 81 |
| $200 \mathrm{E}+02$ | $694 \mathrm{E}+0$ | -3 44E+02 | $787 \mathrm{E}+02$ | $391 E+01$ |  | $6 \mathrm{BCE}+00$ | $438 \mathrm{E}-03$ | 2.48E-02 | 128E+03 | 2 62E-03 | -9 40E-0 | 208 E | -7 53E-08 | 2 82E-02 | $272 E$ | - 82 |
| 1.59E+02 | 6 96E+03 | - 30 E+02 | 7.89E | $497 \mathrm{E}+01$ |  | C 40 | 3 31E-03 | 1.86E-02 | 9 98E+02 | $248 \mathrm{E}-03$ | -73E-03 | 248 E | - 74E | $317 \mathrm{E}-02$ | 482 | -1 31E+02 |
| 1.28E+02 | $698 \mathrm{E}+0$ | $-551 E+02$ | $791 \mathrm{E}+02$ | $625 E+01$ |  | 1.09E+01 | $271 \mathrm{E}-03$ | $155 \mathrm{E}-02$ | 7 93E+02 | $2.22 \mathrm{E}-03$ | $\rightarrow$ T4E-03 | 2 80E | -5 90E-06 | 3 35E-02 |  | 73 |
| $1.00 E+02$ | $701 \mathrm{E}+03$ | - $87 E+02$ | 7 95E+02 | 7.79E+01 |  | $143 \mathrm{E}+01$ | $2.27 \mathrm{E}-03$ | 1.24E-02 | - $30 \mathrm{E}+02$ | $189 \mathrm{E}-03$ | - SME-03 | 3006 - | -5 30E-06 | 3 98E-02 | 1.28E+ | -2 27 E |
| 7.06E+01 <br> © 32E+01 | 7.04E+03 <br> $7.08 \mathrm{E}+03$ | --4.4E+02 | $708 \mathrm{E}+0$ $803 \mathrm{E}+0$ | - $58 E+01$ $188+02$ |  | $1.78 \mathrm{E}+01$ | $1.88 \mathrm{E}-03$ | 1.01E-02 | $500 \mathrm{E}+02$ | 1 161E-03 | -2 45E-03 | 321 E | 4 90E-0 | $447 \mathrm{E}-02$ | $187 E$ | 227 |
| $502 \mathrm{E}+01$ | $7.17 \mathrm{E}+03$ | -1 $31 \mathrm{E}+03$ | $813 \mathrm{E}+02$ | 149 E |  |  |  |  |  | 1.40 | -1 70E-03 | 3 52E | 442 | 502 E .02 | 2.77 E | S 40E+02 |
| 3 99E+01 | 7.19E+03 | -1.56E+03 | 5 16E+02 | 1.77E+02 |  | 3.22E+01 | 1.41E-03 |  |  |  |  | 2.78 |  | $583 \mathrm{E}-02$ | 832 E | -567 |
| 3.17E+01 | 7.29E+03 | $-1.96 \mathrm{E}+03$ | 8.26E+02 | $222 \mathrm{E}+02$ |  | 4 | 8.08EE-04 | 431 E | $251 E+02$ | 103 L | $\rightarrow 91 \mathrm{E}-0$ | 412 E | -35 | 32E-02 | 565 | 4.79E+02 |
| 2 52E+01 | 7.38E+03 | -2 40E+03 | $837 \mathrm{E}+$ | 272 E |  | 862 E | 7.27E-04 | 4 52E | . 89 | 900 | -4 89E-04 | 458 E | 248 E .06 | $709 \mathrm{E}-02$ | 4.53 | 4 50E 02 |
| 2.00 E | 7 49E+03 | -2.93E+03 | $849 E+02$ | 332 E 02 |  | 8 S6E+0 | $597 \mathrm{E}-04$ | 2.88E-03 | 1.20E+02 | 7.15 | 3.15 |  |  | 7 95E-02 | 1.00 | 25E+02 |
| $1.59 \mathrm{E}+0$ | 7.63E+03 | -3.58E+03 | 8 65E+02 | 4.08E+02 |  | $843 \mathrm{E}+0$ | $4.80 \mathrm{E}-04$ | $2.36 \mathrm{E}-03$ | 9 98E+01 | S AIE-S | -1 10E-04 | 864 | 1.53E | 02 |  |  |
| 1.26E+01 | $779 \mathrm{E}+03$ | - $498 \mathrm{E}+0$ | $8 \mathrm{BEE}+6$ | $498 E+02$ |  | 1.03 E | 4 OOE-04 | 1.93E-03 | 7.03E+01 | $583 \mathrm{E}-04$ | - 0 E-05 | 7.35 | ${ }^{3} 16$ | 1.12E-01 | $1.70$ |  |
| 1 O0E+01 | $801 \mathrm{E}+03$ | S 37E+03 | 9.00E+02 | $609 E+02$ |  | 1.28E+ | 3.30E-04 | 1.57E-03 | - 30E+01 | 3.34E-04 | + 33E-08 | \% 48 | . 148 | . 12 E | 1.17 | ,47E02 |
| $7.96 \mathrm{E}+00$ | 8.29E+03 | -50E+03 | 9 90E+02 | 7 46E+02 |  | 1.60E+02 | 2.74E-04 | 1.28E-0 | $500 E+01$ | $4.95 E-94$ | 1.61E-05 | 9 90E-00 | 323 E .07 | 1.4 E- | 2 02E403 | 6. |
| 6.32E+00 | 8 65E+ | -605E+03 | 9.81E+02 | 9.13E+02 |  | $2.00 E+02$ | 2.29E-04 | 1 OUE-03 | 3 07E+01 | 4.65E-04 | 3.13E-05 | 1.17E-05 | 787E-07 | $150 \mathrm{E}-01$ | 2.14E-03 | 1.44E+02 |
| $5.02 \mathrm{E}+00$ | 9.12E+0 | $\rightarrow 84 \mathrm{E}+03$ | $103 \mathrm{E}+03$ | $1.12 \mathrm{E}+03$ |  | 2 54E402 | 1.04E-04 | 8 52E-04 | 3.16E+01 | 4 $412 \mathrm{E}-4$ | 4 OME-05 | 1 4OE.05 | $128 \mathrm{E}-08$ | 1.7EE-01 | $225 E+03$ | $2.07 E+02$ |
| $\begin{aligned} & \text { 3.99E+00 } \\ & \text { 3 } 17 E+\infty 0 \end{aligned}$ | $\begin{aligned} & 973 \mathrm{E}+03 \\ & 1.05 \mathrm{t} \end{aligned}$ | -1.20E+04 | $1.10 E+03$ 1.19E+03 | 1.36E+03 <br> 1.65E+03 |  | 3.23E+02 | 1.65E-04 | 0.95 E | $2.515+01$ | 4.22E-04 | 4 COE-05 | 1.68E-03 | 1.83E-08 | $200 \mathrm{E}-01$ | 23 LE 03 | 255 E -02 |
| 2.52E+00 | 1.16 | -1.77E+C | 1.31E+03 | 2.01E+03 |  | 4.12E+02 | 1.42E-04 | 569E |  | 408 E | ${ }^{4}$ DOE-05 | 2.04E-05 | 2.46E-06 | $224 \mathrm{E}-01$ | $243 \mathrm{Ec03}$ | 2.83 |
| $2.00 \mathrm{E}+\infty$ | 1.29E+04 | -2.15E+04 | 148 E 03 | $2.43 E+03$ |  | 6.79E+02 | $1.065-04$ | 3. 1 IE-0 | 1.28 E |  |  |  | 3.26 E | 2516.01 | $251 E+03$ | 3.30E+02 |
| 1.59E+ | $146 E 40$ | -2 59E+04 | 1.65E+03 | 2.94E403 |  | $6.70{ }^{\text {c }}$ | $928 E-05$ | 3 13E-04 |  | 3.71E-04 | 584 | 37 | $427 \mathrm{E}-06$ 385 E | $212 E-01$ $317 E-01$ |  | 36 |
| $1.28 \mathrm{E}+\infty 0$ | 1 67E+0A | -311E+04 | $1.90 \mathrm{E}+03$ | 3.53E+03 |  | $1.12 E+03$ | $817 \mathrm{E}-5$ | $2.50 \mathrm{E}-04$ | 7.93E+00 | 3.60E-04 | 5 coe-os |  |  |  |  |  |
| $1.005+00$ | $1.95 \mathrm{E}+0$ | $3.72 \mathrm{E}+04$ | 2.21E+03 | 4.22E+03 |  | 143 E 03 | 7.22E-05 | 2.13E-94 | 8.30E+00 | 3 S0E-94 | 8 O9E-05 | 6 SAE-05 | 7.07E-08 | 3. $3.98 \mathrm{EE-01}$ | 2.7eE+03 | $422 E-02$ $485+02$ |
| $7.96 \mathrm{E}-01$ | 2275 | -43E+04 | 2 57E+03 | 5.03E+03 |  | $1.79 \mathrm{E}+03$ | 6296.05 | 1.77E-04 | $500 E+\infty$ | $341 E .04$ | -17E-0S | $8815-05$ | $123 \mathrm{E}-08$ | 4 47E-01 | 2. 2 CEE +03 | 14E+02 |
| C.32E-01 | $2.71 \mathrm{E}+0$ | 5.27E+04 | 3.07E+03 | $598 \mathrm{E}+03$ |  | $2.29 E+03$ | 8.59E-05 | $146 E$ | $397 E+00$ | $327 E-04$ | © 34E-0S | 2.24E-05 | $1.60 \mathrm{E}-05$ | $802 \mathrm{E}-01$ | 2 SUE+0S | 6.70E+02 |
| $502 \mathrm{E}-01$ | 3.22E+0 | -6 23E+04 | 3.06E+03 | 7.07E+03 |  | $288 \mathrm{E}+03$ | 4 04E-03 | $121 \mathrm{E}-\mathrm{A}$ | 3.16E+C0 | 3.18E-04 | fece-0s | 1.01E-04 | $212 \mathrm{E}-05$ | C3E-01 | s O1E+03 | 1 $116+02$ |
| 3.99E-01 | $3.84 \mathrm{E}+04$ | -7.31E+04 | $4.35 \mathrm{E}+03$ | $830 E+03$ |  | $3.57 \mathrm{E}+03$ | 4.38E-OS | $1.02 \mathrm{E}-04$ | $2.51 \mathrm{E}+\infty$ | 3 O8E.04 | 8 cce-0s | 1.22E-04 | $274 E-05$ | 32E-01 | J1EE+03 | 6.00E +02 |
| $3.17 \mathrm{E}-01$ | $488 \mathrm{E}+04$ | - 53E+04 | $531 \mathrm{E}+03$ | 9.60EE03 |  | $453 \mathrm{~F}+03$ | 3 98E-05 | $847 E-05$ | $109 E+00$ | 2 06E-04 | $702 \mathrm{E}-05$ | 1.48E-04 | 353 E -5 | 7 Oex.01 | $3206+03$ | ${ }^{1} 18+02$ |
| $2.52 \mathrm{E}-01$ | $581 \mathrm{E}+04$ | -1 00E+05 | $637 \mathrm{E}+03$ | 1.14E+04 |  | $559 \mathrm{E}+03$ | $3.47 \mathrm{E}-05$ | 7.08E-05 | $186 E+\infty$ | 2 E3E-04 | 7.03E-03 | 1.70E-04 | 4 44E-0S | 7 OSE-01 | j 33E403 | 17E-02 |
| $\begin{aligned} & 2 \text { 200E-01 } \\ & 159 E-01 \end{aligned}$ | 673E+04 | -1.17E+05 | $7.85 E+03$ $899 E+03$ | $1.33 E+04$ $1.53 E+04$ |  | $6.87 \mathrm{E}+03$ | 3.06E-05 | 8 93E-05 | 1.288+ +0 | 2 88E-04 | 7 00e-0s | 2.14E-94 | 5 04E-05 | $102 \mathrm{E}-01$ | $3486+03$ | 20E-02 |
| $\begin{aligned} & 159 \mathrm{E}-01 \\ & 126 \mathrm{E} \end{aligned}$ |  | $\begin{aligned} & -134 E+05 \\ & -1.56 E+05 \end{aligned}$ | 8 99E+03 | 1.53E+04 |  | $8.21 \mathrm{E}+03$ | $2.74 \mathrm{E}-05$ | 5.08E-05 | 9 98E-01 | 2 S1E-04 | 7.12E-05 | 2.51E-04 | 7.13E-03 | $1006+\infty$ | 3 C0E 03 | $1.05 \mathrm{E}+03$ |
| 1.00E-01 | - |  |  | 1.77E+04 |  | $1.00 \mathrm{E}+04$ | 2.43E-05 | 4 28E-05 | 7.03E-01 | 2 37E-04 | 748 E .05 | 209 EOH | - 43E-05 | 1.12E+00 | 3 ME.03 | 1.21E-03 |
|  |  |  |  |  |  | 1.39E+04 | $244 \mathrm{E}-05$ | $341 E-05$ | 628 E | 2 23E-04 | $754 \mathrm{E}-05$ | 3.55E-04 | 1.20E- | $128 \mathrm{E}+\infty$ | 402 E | 1.36E |

$\begin{array}{ccc}-508 E+00 & -1.14 E-03 & -282 E-02 \\ -13 E+00 & -8 & 07 E-03\end{array}+35 E-02$

$1.28 \mathrm{E}+03705 \mathrm{E}+03 \quad 1.05 \mathrm{E}+02000 \mathrm{E}+02 \mathrm{e}-1.19 \mathrm{E}+01$ $\begin{array}{llll}1.00 \mathrm{E}+03 & 7.07 \mathrm{E}+03 & 236 \mathrm{E}+01 \\ 7 & 802 \mathrm{E}+02 & -267 \mathrm{E}+00\end{array}$
 $\begin{array}{llll}6.32 \mathrm{E}+02 & 7.12 \mathrm{E}+03 & -1 & 07 \mathrm{E}+02 \\ 5.02 \mathrm{E} & 07 \mathrm{O} & 7.07 & 1.21 \mathrm{E}+01\end{array}$ 3.99E+02 7.18E+03-2.47E+02 © $14 \mathrm{E}+02 \quad 2.80 \mathrm{E}+01$ $3.17 \mathrm{E}+027.21 \mathrm{E}+033.18 \mathrm{E}+02$ : $18 \mathrm{E}+02 \mathrm{3} 31 \mathrm{E}+01$ $2.52 \mathrm{E}+02 \mathrm{7.25E}+03-3.95 \mathrm{E}+02 \mathrm{~B} 22 \mathrm{E}+02 \mathrm{4} 46 \mathrm{E}+01$ $200 E+02729 E+03-4.75 E+02827 E+02830 E+01$ $159 E+027.33 E+03-570 E+02: 32 E+02 \quad 647 E+01$

 $6.32 \mathrm{E}+017.60 \mathrm{E}+03-1.13 \mathrm{E}+03$ 8 $61 \mathrm{E}+02 \quad 1.28 \mathrm{E}+02$ $502 \mathrm{E}+017.65 \mathrm{E}+03-1.37 \mathrm{E}+03867 \mathrm{E}+02 \quad 3.55 \mathrm{E}+02$ $300 \mathrm{E}+017.62 \mathrm{E}+03-1.59 \mathrm{E}+03867 \mathrm{E}+02 \quad \mathrm{I} .1 \mathrm{E} \mathrm{E}+02$ $\begin{array}{lllll}3.17 E+01 \\ 2525+09 & 7.96 E+03 & -1.49 E+03 & 03 E+02 & 2.14 E+02\end{array}$ $\begin{array}{lllll}200 E+01 & \text { i } & 37 E+03 & 2.65 E+03 & 9 \\ 2 & 49 E+02 & 300 E+02\end{array}$ 1.50E+01 0 85E+03-3.13E+030 81E+02 3. $35 \mathrm{E} E+02$

 $1.00 \mathrm{E}+010.47 \mathrm{E}+03-122 \mathrm{E}+031.07 \mathrm{E}+03 \quad 4.00 \mathrm{E}+02$ $\begin{array}{llll}7.00 E+00 & 1.01 E+04 & -6.03 E+03 & 1.14 E+03 \\ 5.70 E+02\end{array}$ | $6.32 \mathrm{E}+00$ |
| :--- |
| $5.02 \mathrm{E}+00$ |
| $1.08 E+04$ |
| $175 \mathrm{E}+04$ |



 $252 \mathrm{E}+001.56 \mathrm{E}+04+56 \mathrm{E}+03177 \mathrm{E}+03 \because 71 \mathrm{E}+02$ $2.00 \mathrm{E}+001.72 \mathrm{E}+04+897 \mathrm{E}+031.94 \mathrm{E}+03 \mathrm{I}$ 1.02E+03 $1.50 \mathrm{E}+001.87 \mathrm{E}+04+28 \mathrm{E}+03212 \mathrm{E}+03105 \mathrm{C}+03$ $1.28 E+00 \quad 2.03 E+04 \rightarrow 42 E+032.31 E+03 \quad 107 E+03$ \begin{tabular}{llll}
$100 E+00$ \& $218 E+04$ <br>
$706 E-01$ \& $233 E+04$ \& $56 E+03$ \& $247 E+03$ <br>
\hline

 

6 <br>
6 \& $32 E-01$ \& $248 E+04$ <br>
\hline
\end{tabular} $502 \mathrm{E}-01261 \mathrm{E}+04$ - $72 \mathrm{ZE}+032$ 206E+03 $1.10 \mathrm{E}+03$ 3 09E-01 2.75E+04 -0 94E 033 3.11E+03 1.13E+03

 $252 E-013.03 E+04-103 E+043.43 E+03 \quad 1.17 E+03$ 2.00E-01 $3.19 E+04-108 E+04362 E+03 \quad 1.22 E+03$
 1.00E-01 $360 \mathrm{E}+04 \mathrm{~F}$-1.32E+04 4 18E+03 $1.40 \mathrm{E}+03$


| $180 \mathrm{E}+00$ | $4.71 \mathrm{E}-02$ | $160 \mathrm{E}-01$ |
| :--- | :--- | :--- | :--- |
| $487 \mathrm{E}+00$ | 285 E | 71 |

$\begin{array}{cccc}487 E+00 & 285 E-02 & 7 \text { 10E-02 } \\ \\ 7.97 E+00 & 1.70 E-02 & 430 E\end{array}$
$\begin{array}{lll}7.97 \mathrm{E}+00 & 1.70 \mathrm{E}-02 & 4.30 \mathrm{E}-02 \\ 1.13 \mathrm{E}+01 & 1.24 \mathrm{E}-02 & 107 \mathrm{E}-02\end{array}$
$\begin{array}{llll}1.13 E+01 & 1.24 \mathrm{E}-02 & 1.307 E-02 \\ 1.53 \mathrm{E}+01 & 0 & 96 \mathrm{E}-03 & 235 \mathrm{E}-02\end{array}$
$\begin{array}{llll}1.95 E+01 & 82 E-03 & 2.35 E-02 \\ 1.26 E+01 & 20 E-03 & 1.07 E-02\end{array}$
$245 \mathrm{E}+01$
$202 E+01$
$3.50 E+01$



| 4 SSE 01 |
| :--- |
| 5 SEE |




| $14 E+01$ | $2.11 E-03$ | $8.48 E-03$ |
| :--- | :--- | :--- |
| $5 S E-03$ |  |  |

1.01E+02 $1.00 E-03 \quad 3$ B3E-03
1.78E+02
$\begin{array}{llll} & 1.10 E+02 & 1.13 E-03 & 2.25 E-03 \\ 033 E-04 & 105 E-03\end{array}$
2.71E+02
$3.36 E+02$



$\begin{array}{cccc}8 & 03 E+02 & 847 E-04 & 1.4 E-04 \\ 9 & 17 E+02 & 8.15 E-04 & 8.97 E-04\end{array}$
$\begin{array}{cccc}9 & 97 E+02 & \text { E.15E-04 } & 8.17 E-04 \\ \text { 1.14E+03 } & 480 E-04 & 435 E-04\end{array}$
1.32E+03 $464 E-043$ S0E-04
$\begin{array}{lll}1.50 E+03 \\ 1.87 E+43 & 4.42 E-04 & 3.14 E-O 4\end{array}$

| $167 E+03$ |
| :--- | :--- |
| $1.421 E-04$ |
| $2.73 E-04$ |


$\begin{array}{lll}2.15 E+03 & 3.68 E-04 & 2.09 E-04 \\ 2.86 E-04 \\ 2.31 E+03 & 30 E-04 & 170 E-04\end{array}$

$\begin{array}{lll}203 E+03 & 3.16 E-04 & 1.41 E-04 \\ 201 E+03 & 200 E-04 & 1.30 E-04\end{array}$
$\begin{array}{llll}3022 E+03 & 2.78 E-04 & 1.22 E E-04 \\ 3.18 E+03 & 204 E-04 & 1.105 E-04\end{array}$
$\begin{array}{lll}3.16 E+03 & 2.61 E-04 & 1.18 \mathrm{E}-04 \\ 3.38 E+03 & 247 E-04 & 1.09 E-04\end{array}$




| quency | $z$ | Z $1 \mathrm{~cm}^{2}$ | Z"/cm ${ }^{8}$ | R | Rs | $r$ | r |  |  |  | r |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $200 E^{+03}$ | 677 E | $780 \mathrm{E}+0$ | SsE+ |  | 3.31E |  | $277 \mathrm{E}-02$ |  | 33E |  | -1 |  | 4/sart(w) | $\begin{gathered} \text { ( }(\mathrm{s}) \\ -2 \text { lef+02 } \end{gathered}$ |  |
| $159 \mathrm{E}+03$ | 67EE+03 $217 \mathrm{E}+02$ | $7{ }^{\text {c }} 8 \mathrm{EE}+0$ | -2 48E+01 |  | $275 \mathrm{E}$ |  | $-401 E-02$ | $\begin{aligned} & 8.28 E+04 \\ & 898 E+03 \end{aligned}$ | $\begin{aligned} & -233 E . \\ & -606 E . \end{aligned}$ | $\begin{aligned} & -232 E-03 \\ & -722 E-03 \end{aligned}$ | $\begin{aligned} & -186 \\ & -607 \end{aligned}$ | $\begin{aligned} & -184 E-07 \\ & -723 E-07 \end{aligned}$ | $\begin{aligned} & 602 E-03 \\ & 100 E-02 \end{aligned}$ | $\begin{aligned} & -2 \text { reEA } \\ & \hline \end{aligned}$ |  |
| $\begin{aligned} & 128 E+03 \\ & 400 \mathrm{~F}+03 \end{aligned}$ | 179E+03 1.29E+02 | $770 E+02$ $7>1 \mathrm{E}+02$ | -1 47E+01 |  | $-194 E$ | $190$ | 71E-02 | $7 \text { E3E } 0$ | -1.2be | S 33E-02 | -162 | - -2 20E-07 | 1 12E-02 | Ste |  |
| $400 \mathrm{t}+03$ <br> 7 96E +02 |  | 7.71E+02 | -5 82E+00 |  | $6.90 \varepsilon$ | (e) | - CSE-01 |  |  |  |  |  |  |  |  |
| $7 \text { 98E }+02$ $832 E+02$ | $881 E+03-203 \mathrm{E}+01$ $6 \text {-2E+03-21E+01 }$ | $7.72 \mathrm{E}+02$ $774 \mathrm{E}+02$ | $230 \mathrm{E}+00$ $315+\infty$ |  | $493 E-01$ | $888 \mathrm{E}-02$ | $415 \mathrm{E}-01$ | 800 | +13E | - 3 11E-01 |  |  | 141 l | $218 E-02$ $100-01$ |  |
| $\begin{aligned} & 632 E+02 \\ & 502 E+02 \end{aligned}$ | $682 E+03-421 E+09$ | 774E+02 | $31 \mathrm{E}+00$ $175 \mathrm{E}+01$ |  | $208 E+00$ | 2.28E-02 | 1.02E |  |  | -41E-02 |  | 05 | 1 S0E-02 | 173 |  |
|  |  | 7.75E+02 | 1.75E+01 |  | $303 \mathrm{E}+00$ | $123 \mathrm{E}-02$ | 5 45E-02 | $318 \mathrm{E}+03$ | B4E. | -1 88E-02 |  |  | 17 BE-02 | 242 |  |
|  | ( 86E+03-2 20E+02 | 7.78E 02 | 2 60E+01 |  | ${ }^{6} 11 E+\infty$ | - 59E-03 | 3 65E-02 |  | 1 6eE | $1046-02$ | $\mathrm{C}_{61}$ | $417 \mathrm{E}-\infty$ | 2006.02 | 140 |  |
| 3 17E+02 <br> $252 \mathrm{E}+02$ | 6 68E+03 -3 10E+02 | $7.80 E+02$ $783 E+02$ | $351 \mathrm{E}+01$ |  | 6 62E+C0 | 6 59E-03 | 2 68E-02 | 189 | 1.77E-0 | C0E-03 | 8 8 | 3 31E-06 | 2 24E-02 | 376 |  |
| 2 52E+02 <br> 2 00E 02 | $691 E+03-397 E+02$ $693 E+03-497 E+02$ | 7.83E+02 $786 E+02$ | $450 E+01$ 5 $53 E+01$ |  | $116 \mathrm{E}+09$ | $537 \mathrm{E}-03$ | $208 E-02$ $108 E-02$ | 1.58E+03 | 175 E | $\rightarrow$ S4E-03 | 111 |  | 2 SIE-02 | 73 |  |
| $1.59 \mathrm{E}+02$ | $697 \mathrm{E}+03$ - 16E+02 | 7 90E+02 | 8 PeE +01 |  | 1.47 CH 01 | $435 E-03$ 3 50E-03 | ( 1 coE-02 | 1.28E+03 | 1 6月E | -3 10E-03 | 131 E | -2 47 | $282 \mathrm{E}-02$ | 131 |  |
| $126 \mathrm{E}+02$ | $701 \mathrm{E}+03$-7 53E+02 | 7.95E+02 | B SaEfot |  | 2 MEPO1 | 2 09E-03 | 1 O9E-02 | 7 93E+02 | 1.33 |  |  | - 2 15E-00 | $317 E-02$ | 2.10 E |  |
| $100 \mathrm{E}+02$ | $706 \mathrm{E}+03-18 \mathrm{E}+02$ | $500 \mathrm{E}+02$ | $104 \mathrm{E}+02$ |  | 2 89E+01 | 2 49E-03 | $894 \mathrm{E}-03$ | $630 \mathrm{Et02}$ |  | -03E-04 |  |  |  |  |  |
| $7.96 \mathrm{E}+01$ | 7.12E+03-11 1E+03 | $107 \mathrm{E}+02$ | 1.28E+02 |  | 3 30E+01 | 2.10E-03 | 7 3ME.03 | $5006+02$ | 1.03E-0 | - 58E-04 | $207 E$ | -1 58E-06 | 3 38E-02 |  |  |
| $632 \mathrm{E}+01$ | 7.19E+03 -1.35E+03 | $815 \mathrm{E}+02$ | $153 \mathrm{E}+02$ |  | 4 39E+01 | 1.74E-03 | 6 O5E-03 | 3 97E+02 | - 11 E-9 | -4.06E-04 | 2 20E | -1.02E-06 | S O2E-02 | 015 |  |
|  | 7.26E+03 -1.57E+03 | $324 \mathrm{E}+02$ | 1.78E+02 |  | $822 \mathrm{E}+01$ | ${ }_{1}^{151 E-03}$ | $516 E-03$ | 3 10E+02 |  | -5SE-94 | 2.10 E | -1.76E-08 | 5 E3E-02 | 187 |  |
| $317 \mathrm{E}+$ | 7.50E+03-236E+03 | Iste+ | 222 E |  | 653 E | $122 \mathrm{E}-03$ | 4 15E-03 | $2.51 \mathrm{E}+02$ |  | -1.37E-04 | 2 15 | 648E-07 | ( $32 \mathrm{E}-02$ | 1.35 |  |
| 2 52E+01 | $764 \mathrm{E}+03$-2.85E+03 | 187E+02 | 3.23E+02 |  | - SOEFOT | - S6E-04 | 285 L |  | 8 | -5 26E-05 | 324 C | 2 OAE.07 | 7.00E-0 | 18 |  |
|  | $7.82 \mathrm{E}+03-3.45 \mathrm{E}+03$ | $386 \mathrm{E}+02$ | $381 \mathrm{Et02}$ |  | 1. $15 \mathrm{E}+02$ | 6 O1E-04 | 2 35E-03 | $1.26 \mathrm{E}+02$ | 528 E - |  |  | $\begin{array}{r}-320 E-00 \\ \\ \hline\end{array}$ | 195 C |  |  |
| 1.59E+ | $103 \mathrm{E}+03$-4.18E+03 | 2.10E | $474 \mathrm{E}+02$ |  | 1 30E+02 | $570 \mathrm{E}-04$ | 1.94E-03 | 9 PeE+01 | 4 83E.04 | \$82E-05 | 4 S4E-09 | 5 63E-07 | 1.00 E .01 |  |  |
| $1.26 \mathrm{E}+01$ | - 30E+03 -5.06E+03 | - 41E+02 | 5.74E+02 |  | $170 E+02$ | 4.74E-04 | 1.60E-03 | 7 93E+01 | 4.46E-0 | 8 83E-05 | 8 62E-00 | B EIE-07 | $112 \mathrm{E}-01$ | $2.10 \underbrace{403}$ |  |
| $1.005+01$ | 8 64E+03 -6.12E+03 | - 80E+02 | 6 O4E+02 |  | 208 E 02 | $398 \mathrm{E}-04$ | 1.32E-03 | ( 30E+01 | 4.14E-04 | 7 30E-05 | S Sek-0 | 1.18E-0 | 1.26E01 | 2 3ME 0 OS | ${ }^{4} 13 \mathrm{E}$ |
|  | 9.07E+03 -7.40E+03 | 1.03E+03 | 8.39E+02 |  | 2 57E+02 | 3.33E-04 | 1.09E-03 | 3.00E+01 | 3 00E-04 | 7.28E-05 | 7.60E-08 | 1.45E-0 | 1.41E-01 | 2 48E003 | 4 coe |
| 6 32E +00 | 9 46E 03 -7.79 | 107 E | $897 \mathrm{E}+02$ |  | $301 \mathrm{E}+02$ | $278 E-04$ | 9 10E-04 | $397 E+01$ | 3.77E-0 | 472 E -05 | - 48E-08 | 1.10E-06 | 1 S0E-01 | $261 E+03$ | 3.2 |
| $5.02 \mathrm{E}+00$ 3 09E 400 | $1 \begin{aligned} & 103 E+04-1.07 \mathrm{E}+04 \\ & 108 \mathrm{t}+04 \\ & -125 \mathrm{ta}\end{aligned}$ | 1.17 E | $1.22 E+03$ $.142 E+03$ |  | $308 E+02$ $451 E+02$ | $241 \mathrm{E}-04$ | 7 42E-04 | $318 E 401$ | $357 \mathrm{E}-04$ | C08E-05 | 1.13E-05 | 1 12E-00 | 1.78E-01 | $272 \mathrm{ta3}$ |  |
| $3.17 \mathrm{E}+00$ | 1.20E+04 -1.53E+04 | 1.36E+03 | 1.73E+03 |  |  |  |  |  | 3 S0E.04 SOE.O4 | 3.20E-05 | 1 40E.0S | 1.28E.00 | 2 00E-01 | $283 \mathrm{E}+03$ |  |
| $252 \mathrm{E}+00$ | 1.33E+04 -1.82E+04 | 1.51E+03 | 2.07E+03 |  | 7 40E 02 | 1.53E-04 | 429 E -0 | 15 |  | $4.18 E-05$ <br> OAE-05 | 1.71E-0s <br> $209 \mathrm{E}-05$ | $2.10 E-06$ 2 SSE-0 | $224 \mathrm{E}-01$ | 2.00E+03 |  |
| 2.00 E | 1.40E+04-2 16E+04 | $109 \mathrm{E}+03$ | $245 E+03$ |  | $018 \mathrm{E}+02$ | 1.3E-S4 | 3 SeE-04 | 1.28E+01 | 324 E - | 3 TE-OS | S0E-05 |  |  | 2 80E*03 3 O4E |  |
| $159 \mathrm{E}+00$ | E+04-2 55E+ | 2.00E+03 | 2.89E+03 |  | 123 E 03 | 1.24E-04 | 2 03E-04 | - 98E+00 | 3 10E-04 | $427 \mathrm{E}-03$ | 3.10E-05 | $427 \mathrm{E}-08$ | 3.17E-01 | 3.17 |  |
| $128 \mathrm{E}+00$ | $203 \mathrm{E}+04$ S OSE+04 | 2.30E+03 | 3 45E+03 |  | 1.53E+03 | 1 07E-04 | 2 42E-04 | 7 93E+00 | 307 E | 4 S0E-OS | 3 B7E-05 | 8 67E-06 | 3 55E-01 | 3.19E 09 |  |
| OOE +00 | $2.37 E+04$ 3.56E+04 | $2.69 \mathrm{E}+03$ | 4.04E+03 |  | $192 \mathrm{E}+03$ | - 50E-03 | $202 \mathrm{E}-04$ | 6.30E+00 | 3 00E-04 | 4 S0E-0S | 4 T7E-05 | 7.15E-00 | 3 OBE-01 | $3208+03$ |  |
| 96E-01 | 2.83E+04 - $4.18 \mathrm{E}+04$ | 3.21E003 | $474 E \cdot 03$ |  | 2 43E+09 | : 50E-0S | 1 87E-04 | 5 00E+00 | 2.83E-9 | 4.09E-05 | 8 SSE-05 | 1 37E-0 | 4 47E-01 | 3 33E+03 |  |
| 6.32E-01 |  | $361 E+03$ | $547 \mathrm{E}+03$ |  | $284 \mathrm{E}+03$ | $747 \mathrm{E}-05$ | 1.44E-04 | 3 97E+00 | 2 90E-04 | 4 25E-05 | 7.30E-05 | 1.07E-05 | 802 E .01 | 3 37E+03 | 10 |
| 3 99E-01 | 4.3E+04 - 52 S | 4.22 E | 7.38 |  | $347 E+03$ | \% S0E-05 | 120E-0 | $318 E+00$ $251 E+\infty$ | $282 E-04$ | 4 70E-0S | $194 E-0 s$ | 140E-05 | 8 83E-01 | 3 45E-03 | 6. 7 |
| $317 \mathrm{E}-01$ | S01E+04 -7 45E+04 | 5 CoE+03 | $344 \mathrm{E}+03$ |  | $491 E+03$ | 5.15E-05 | ${ }^{8} 8$ |  | $275 \mathrm{E}-0$ 2.70 e | 4.57E-0S | q.10E-04 1 $135 E-04$ | $1.82 E-05$ $244 E-05$ | 32E-01 | 3 SAE 0 OS | (1) |
| 2 52E-01 | 624E+04 -0 4SE+04 | 7 08E+03 | 1.07E+04 |  | - $31 \mathrm{E}+03$ | 4 O0E-05 | C P3E-05 | 1.50E |  |  |  | 344 CE | 7 \%05E.01 | $350 e^{+03}$ 9 coe 03 |  |
| $2.006-01$ | $737 \mathrm{E}+04-8.03 \mathrm{E}+04$ | 3.35E+03 | $101 \mathrm{E}+04$ |  | $758 \mathrm{E}+03$ | 4.74E-05 | 6 33E-05 | 1.28E+00 | 2 40E-04 | 8 OUE-05 | 105 | 4.01E-0S | 0 02E-01 | 301 Ecos |  |
| $159 \mathrm{E}-01$ | $830 \mathrm{E}+04-1.13 \mathrm{E}+05$ | $941 E+03$ | 128 E |  | 8 64E+03 | 362E-03 | \$ 37E-05 | - 08E-01 | 2 40E-04 | 8 OTE-05 | 2 40E.0 | soze-0s | $1006+00$ |  |  |
| $1.26 \mathrm{E}-01$ | $972 \mathrm{E}+04-1.28 \mathrm{E}+05$ | 110 E | 1.45E+04 |  | $102 \mathrm{E}+04$ | 3.25E-05 | 4 C0E-0S | 7.03E-01 | 2 32E-04 | 8 43E-05 | 2 03E.04 | 6 SUE-0S | $1.12 \mathrm{E}+\infty$ | 400 ecos |  |
|  | 1.15E+05-1.48E+05 | 1.31E+ | 1.65E |  | $123 \mathrm{E}+04$ | 2 00E-05 | 3 00E-05 | $626 E$ | 2 20E. | 552 E | 3 SOE- | 3 70E-05 | $1.26 E$ |  |  | With ET reagent

$-329 E+00+88 E-03-100 E-02$




 | $63 E+02$ | $16 E+03$ | $-143 E+02$ | $12 E+02$ | $162 E+01$ |
| :--- | :--- | :--- | :--- | :--- |
| $5.22 E+02$ | $710 E+03$ | -2 | $17 E+02$ | $16 E+02$ |



 $\begin{array}{llll}200 E+02 & 7.35 \mathrm{E}+03 & -5 & 46 \mathrm{E}+02 \\ 15.34 \mathrm{E}+02 & \mathrm{~S} & \mathrm{Cl} 19 \mathrm{E}+01\end{array}$ $\begin{array}{llll}1.59 E+02 & 7.41 E+03 & -15 E+02 & \text { B } 40 E+02 \\ 1.26 E+02 & 7.40 E+01\end{array}$ $\begin{array}{ccccc}1.20 \mathrm{E}+02 & 7.47 \mathrm{E}+03 & -7.73 \mathrm{E}+02 & \text { \& } 47 \mathrm{E}+02 & 8.77 \mathrm{E}+01 \\ 1.00 \mathrm{E}+02 & 7.54 \mathrm{E}+03 & -1.15 \mathrm{E}+02 & 85 \mathrm{~S}+02 & 1.04 \mathrm{E}+02\end{array}$ $\begin{array}{llll}7.96 E+01 & 7.62 E+03 & -1.00 E+03 & \text { B } 4 E+02 \\ 7.23 E+02\end{array}$ . $32 \mathrm{E}+017.11 \mathrm{E}+03-1.26 \mathrm{E}+03$ 8 $75 \mathrm{E}+02 \quad 1.45 \mathrm{E}+02$ $502 E+01$ 7.85E+03 -1.56E+03 \& $90 \mathrm{E}+022 \mathrm{I}$ 1.77E+02

 \begin{tabular}{lllll}
$252 E+01$ \& 8 \& $14 E+03$ \& $2.10 E+03$ \& $9.24 E+02$ <br>
$240 E+03$ \& $2.30 E+02$ <br>
\hline \& $47 E+02$ \& $282 E+02$

 

$200 E+01$ \& $S 1 E+03$ \& $293 E+03$ \& $87 E+02$ <br>
7 \& $282 E+02$ <br>
\hline
\end{tabular}

 $1.2 \mathrm{EE}+019.34 \mathrm{E}+03-4.05 \mathrm{E}+03 \mathrm{I}, 00 \mathrm{E}+03 \mathrm{~S} 450 \mathrm{E}+02$



 3.17E+00 1.50E+04 +52E+03 1.70E+03 © $68 \mathrm{E}+02$ $252 E+001.05 E+04+00 E+03107 E+03 \quad 103 E+03$ $\begin{array}{llll}2.00 E+00 & 1.81 E+04 & +.52 E+03 & 2.06 E+03 \\ 1.08 E+03\end{array}$
 $\begin{aligned} & 1.28 E+00 \\ & 2.15 E+04 \\ & 1.00 E+98 E+03 \\ & 2.44 E+03 \\ & 1\end{aligned} 13 E+03$
 © $32 E-0 ; 2$ 2 $23 E+04$ - 7 7PE+03 $2.96 E+03$ 1.11E+03 O2E-01 2 7EE+04 + MEE03 3 14E+03 I.13E+03

 $17 E-013.04 E+04+92 E+03344 E+03 \quad 1.12 E+03$ 2.52E-01 $318 E+04+86 E+03962 E+03 \quad 1.12 E+03$ S0E-01 3 $51 E+04-1.05 E+0437 E+03$ I.15E+03 .20E-01 $363 E+04$-1.10E+04 $411 E+03$. $25 E+03$ 1 00E-01 $381 E+04-1.17 E+04432 E+03 \quad 1.33 E+03$ $\begin{array}{llll}225 E+0 & 7.12 E-03 & 1.63 E-02 \\ 2.74 E+01 & 509 E-03 & 1.35 E-02\end{array}$ \begin{tabular}{lll}
2. <br>
3. <br>
\hline

 

4 $01 E+01$ <br>
$4.31 E-03$ \& $943 E-03$ <br>
\hline
\end{tabular} $\begin{array}{lll}\text { 4.80E+01 } & \text { 367E-03 } \\ \text { S.04E-03 }\end{array}$ $5.75 E+011$ 3. $13 E-0386 E-03$

$682 E+01$
2
ESE-0S

S.CAE-03 e.37E+01 2.18E-03 S CBIE-03 | $970 E+01$ | $1.03 E-03$ |
| :--- | :--- |



 $\begin{array}{lll}2.08 E+02 & 1.05 E-03 & 2.30 E-03 \\ 2.00 E-03\end{array}$ $\begin{array}{lll}2.53 E+02 & \text { E 20E-04 } & 1.007 E-03 \\ 312 E+02 & 10 E-04 & 1.50 E-03\end{array}$ \begin{tabular}{lll}
$1.85 E+02$ \& $7.24 E-04$ <br>
I. $1.10 \mathrm{E}-03$ <br>
\hline

 $416+02$ S5E-04 icce-04 

$597 E+02$ \& $890 E-04$ <br>
\hline \& $03 E-04$ <br>
\hline
\end{tabular}

 1.07E+03 4 85E-04 $4.60 \mathrm{E}-04$
 $163 E+03$ C.14E-04 2 STE-O4 1.82E 003 3 $90 E-04247 E-04$

 $231 E+033$ 33E-04 $140 E-04$ $\begin{array}{lll}28 E+03 & \text { S.21E-04 } & 1 \text { ITE-04 } \\ 200 E+03 & 3.08 E-04 & 1.23 E-04\end{array}$ $\begin{array}{lll}200 E+03 \\ 207 E+03 & 293 E-04 & \text { I. } 14 E-04\end{array}$

3.52E+03 2 4PE-04 $42 E-05$






| frequency | z | て" | $2 / \mathrm{cm}^{2}$ | z"/cm ${ }^{2}$ |  | Z'Rs | $r$ | ${ }^{\prime \prime}$ |  |  |  | r | rm/m |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $2.00 E+03$ | $879 E+03$ | 290E+02 | $7706+02$ | 3 30E+01 | $774 \mathrm{E}+02$ | $367 \mathrm{E}+00$ | 316 | 291 | $1285+04$ | $2.48 \mathrm{E}-1$ |  |  |  |  |  | ) |
| 1 S0E+03 | C DOE 403 | $105 E+02$ | $771 \mathrm{E}+02$ | $222 \mathrm{E}+01$ |  | -2 56E +00 | - $14 \mathrm{E}-09$ | 4 4SE-C2 |  |  |  |  |  |  |  |  |
| $128 \mathrm{E}+00$ | $8_{\text {aled03 }}$ | $102 \mathrm{E}+02$ | $772 E+02$ | -1 15E+01 |  | $-152 \mathrm{t}+00$ | 112E-02 | -52E-02 | 7 93E 000 | $214 \mathrm{E}-\mathrm{C}^{2}$ |  |  |  |  |  |  |
| $100 \mathrm{E}+03$ | 6 82E+03 | 1.7TE+01 | $773 \mathrm{E}+02$ | -201E+m |  | -2 12E-01 | -60E02 | 4 82E-01 | [306.03 | 1 11E-01 | $750 \mathrm{E}-01$ | 2005 | $7188 \mathrm{E}-04$ $1196-04$ |  |  |  |
| 7.96E+12 | $683 \mathrm{E}+03$ | -20E+01 | $775 \mathrm{E}+02$ | $703 \mathrm{t}+0$ |  | $114 \mathrm{E}+00$ | $224 \mathrm{E}-\mathrm{O}$ | 1.30E-01 | $5000+03$ | - $33 \mathrm{E}-09$ | -796-02 | 200E-05 | $11965-04$ | $128 \mathrm{E}-02$ | 2 28E-09 | $120 \mathrm{C}+\infty$ |
| $632 \mathrm{E}+02$ | 8 25E+03 | -1 88E+02 | $778 \mathrm{E}+02$ | $213 E+01$ |  | $278 E+00$ | $598 E-03$ | 4 S1E-02 | 397E+03 | 2 S6E-0 | -1 24E-02 | ${ }^{2} .45$ |  | - |  |  |
| $6022+02$ | 6 07E+03 | -2 00E+02 | $779 \mathrm{C}+02$ | 2 95E+09 |  | $512 \mathrm{E}+00$ | $571 \mathrm{E}-\infty 3$ | 3.20e-a | $318 E+\infty$ | $231 \mathrm{E}-03$ | -7.33E-03 | 7 T1E-07 | . 232 E -00 | 1700.0 | 3 300 E +01 | 108 |
| 3 90E+02 | $689 E+\infty 3$ | - 37E+02 | $782 \mathrm{E}+02$ | 3 82E 01 |  | 7 ME +00 | 5.23E-03 | $2.51 \mathrm{E}-02$ | $251 E+\infty$ | 2 03E-0 | -497E-03 | 11E-07 | -1.80E-08 | 2006.02 | 708 E | -1 72E 02 |
| $317 \mathrm{E}+02$ | 6 92E+03 | $422 \mathrm{E}+02$ | $785 E+02$ | $479 \mathrm{ta1}$ |  | 1.13E+01 | 4 85E-03 | 1 19E-02 | $190 \mathrm{E}+\infty$ | 1 82E-03 | 3 36E-03 | $\bigcirc 14 \mathrm{E}-07$ | -1.70E-0 | $224 \mathrm{E}-2$ | $1245+$ | $2206+02$ |
| $252 \mathrm{~F}+02$ | 8 95E+03 | -533E+02 | 7 69E+02 | 5 93E+01 |  | $149 E+01$ | 3.90E-03 | $1506-02$ | $158 \mathrm{E}+03$ | $174 \mathrm{E}-03$ | -2.36E-03 | 1.10e-00 | -1.40E-08 | $251 \mathrm{E}-02$ | $208 \mathrm{E}+02$ | $2756+02$ |
| $2006+02$ | 6 00E+03 | +35E+02 | $703 \mathrm{E}+02$ | 7.20E+01 |  | $195 E+0 \mathrm{~T}$ | 3.50E-03 | $1296-02$ | $128 E+03$ | 1.53E-03 | -1.85E-03 | 1.22E | -1.32E-00 | 2 02E-02 | $302 \mathrm{E}+02$ | - 256.102 |
| $150 \mathrm{E}+02$ | $7.04 \mathrm{E}+03$ | -7 68E+02 | 7.00E 02 | 4 71E+01 |  | $248 E+01$ | $302 \mathrm{E}-33$ | $1065-02$ | - s8E+02 | $138 \mathrm{E}-93$ | -1 11E-03 | 1.30E-0 | -1.11E-0 | $317 \mathrm{E}-02$ | 440E+02 | $3.53 E+02$ |
| $1.26 \mathrm{E}+02$ | $710 \mathrm{E}+03$ | - $91 \mathrm{E}+02$ | 2.05E+02 | $1.06 E+02$ |  | $3.12 \mathrm{E}+01$ | $257 \mathrm{E}-03$ | 871E-03 | 7 93E +02 | 1.21E-9 |  | 1.531 .0 | - $62 \mathrm{E}-07$ | 3 S5E-02 | ( 26E $+\infty$ | S $52 \mathrm{E}+02$ |
| $1006+02$ | $716 E+03$ | -1.12E+03 | $812 \mathrm{E}+02$ | 1.27E+02 |  | $3.88 \mathrm{E}+01$ | $2185-03$ | 7.18E-9 | -30E $+\infty$ | 1.08E-03 | -404E-04 | $1.72 \mathrm{E}-\mathrm{C}$ | -41E-07 | 3 P0E-02 | -12E+02 | - $303 \mathrm{E}+8$ |
| 7 08E+01 | $7.24 \mathrm{E}+03$ | -1.35E+03 | 21E+02 | $153 \mathrm{E}+02$ |  | $478 E+0 ¢$ | 1.87E-03 | 598E-03 | 5.00E $\times 1$ | - 4be-O | $225 E .04$ | 1.80e- | - $400 \in-07$ | $447 E-02$ | - 0 Etica | $237 E+02$ |
| $632 \mathrm{E}+01$ | $7.34 \mathrm{E}+03$ | -1 -2E+03 | $0332+02$ | $1.03 \mathrm{E}+02$ |  | $588 E+01$ | 1.50E-03 | $4956-03$ | $3.97 \mathrm{E} \times 2$ | 28E-04 | -63E-08 | 2.08 E | 2.17E-07 | 802502 | 1.20E +03 | -1.25E*O2 |
| $5028+01$ | 7 70E 03 | $-1.95 \mathrm{E}+03$ | $839 \mathrm{E}+02$ | $221 \mathrm{E}+02$ |  | $557 \mathrm{E}+09$ | $1.24 \mathrm{E}-\infty 3$ | $418 \mathrm{E}-38$ | $316 E+02$ | 8.12E-0 | -174E-04 | $257 \mathrm{E}-08$ | 6.52E-07 | 5 e3E-02 | $1.186+\infty$ | 2676.102 |
| $3 \mathrm{SeF}+01$ | 7 70E+03 | -2.32E+03 | $881 \mathrm{E}+02$ | $284 \mathrm{E}+02$ |  | - $00 \mathrm{E}+07$ | $1.13 \mathrm{E}-03$ | 342E-03 | 2.51E+C8 | S SEE-04 | $691 \mathrm{E}-5$ | $202 E-\infty$ | $238 E-07$ | - 32E-02 | $151 \mathrm{E}+03$ | 1.30E+02 |
| $3.17 \mathrm{E}+01$ | $775 E+03$ | $-2.79 ¢+03$ | : $796+02$ | 3.17E+02 |  | 1 O8E+02 | 9 40E-04 | 2 44E-03 | $150 \mathrm{E}+\infty$ | 8 ent-04 | 1086 -04 | 2.00E-0 | 8.32E-07 | $7.005-02$ | 1 CoEtcos | $301 \mathrm{E}=2$ |
| $2.52 \mathrm{E}+01$ | 7 95E +03 | -35E+03 | $902 \mathrm{E}+\infty$ | 3.00E+02 |  | 1.20E+02 | 7 90E-04 | $2.36 E-03$ | $1.58 \mathrm{E}+\infty$ | 5 23E-04 | 1.25E-04 | $331 \mathrm{E}-\infty$ | 7 BEE-07 | 7 PEE-02 | 1.81E+03 | 431 E 02 |
| $2.005+01$ | $1206+63$ | -4 02E+03 | $930 \mathrm{E}+02$ | 4 SEE+02 |  | $156 \mathrm{E}+02$ | -72E-04 | $1985-03$ | 1.2te $+\infty 2$ | $472 \mathrm{E}-04$ | $133 \mathrm{E}-04$ | 3.75E-08 | 1.08E-08 | $102 \mathrm{E}-02$ | i. $.805+\infty 3$ | S S6E +02 |
| 1.50E+01 | 8.51E+03 | $4.62 \mathrm{E}+03$ | $985 \mathrm{E}+02$ | $547 \mathrm{E}+02$ |  | $1.91 \mathrm{E}+02$ | 5 CoE-a4 | 1 13E-03 | 890E401 | $427 E-94$ | 13 KE-0 | $420 \mathrm{E}-9$ | 1.3E-0s | $100 \mathrm{E}-01$ | $2.13 \mathrm{E}+\infty 3$ | 2 |
| 1.28E+01 | a 90E603 | -5.70E403 | 101E+03 | $658 E+02$ |  | $2356+02$ | $484 \mathrm{E}-4$ | 1.35E-03 | 7 93E 01 | 3 80E-04 | 1.28E-04 | 4.82E-0 | 1.e1E-08 | $112 \mathrm{E}-01$ | $232 \mathrm{E}+03$ | 7.60E.02 |
| $100 \mathrm{E}+01$ | $938 \mathrm{E}+03$ | -93E+03 | 1.06E+03 | 7 85E+02 |  | $2006+02$ | 4.13E-04 | 1.12E-0 | $8306-01$ | 3 62E-04 | 1.17E-04 | $574 \mathrm{E}-06$ | 1.08E-08 | 1380 | $2.50 E+\infty 3$ | 4.006402 |
| $7.96 E+\infty$ | 9 90E+03 | -27E+03 | 1.13E+03 | - 38E+02 |  | $3505+02$ | $356 E-04$ | 9 30E-04 | 500 Etar | 3 30E-0r | $105 E-04$ | C 78E-08 | 2100.00 | 1.41E-91 | 200E+03 | - 31 E402 |
| 6. $32 \mathrm{E}+\infty 0$ | $107 E+04$ | - 8 O4E+03 | $1.22 E+03$ | $112 E+03$ |  | $44 \mathrm{E}+02$ | $300 E-04$ | $773 E-04$ | $397 E+0 r$ | $3.22 \mathrm{E}-04$ | - 25E-05 | C11E-00 | 2.33E-08 | $1.506 \cdot 09$ | $287 \mathrm{E}+03$ | - 25EC02 |
| $502 \mathrm{E}+\infty 0$ | 1.17E+04 | -1 17E+04 | 1.32E+03 | 1.32E+03 |  | 5 50E+02 | 2 6se-04 | - 4EE-O4 | $316 E+01$ | 300E-04 | : OSE-05 | 9.78E-06 | 2 S5E-D | 1.78E-09 | 2.03E 103 | $7205+02$ |
| 3. $906+$ +00 | $1.28 E+04$ | -1.38E+04 | $145 E+03$ | $156 E+03$ |  | 6 E1E 002 | $234 \mathrm{E}-\mathrm{A}$ | $537 \mathrm{E}-04$ | $2.51 \mathrm{E}+\mathrm{O}$ | $2.006-04$ | 7.00E-05 | 1.19E-08 | $283 E-08$ | $2006-01$ | 3.17E+09 | 1.66E 002 |
| $317 \mathrm{E}+\infty$ | 1.42E+04 | -1 62E+04 | $161 E+03$ | 1 8EE+03 |  | 6.37E +02 | $2.05 E-04$ | $450 \mathrm{EO4}$ | 1 190E+01 | 2.00E-04 | 6 13E.06 | 1.40E-05 | 300E-08 | 2246 -09 | $3306+03$ | - $17 \mathrm{E}+02$ |
| $2.52 E+00$ | 1.50E+OA | -1 90E+04 | 1.80E 0103 | $218 E+03$ |  | 1.03E+03 | 1.00E-04 | 3.7TE-04 | $158 E+01$ | $2.448-94$ | 8.41E-05 |  | 3.42E-08 | $251 \mathrm{E}-01$ | 3 40E 103 | ( 485 |
| $2.00 \mathrm{E}+\infty$ | 1.70E+04 | -2.22E+04 | $203 \mathrm{E}+03$ | $2.52 \mathrm{E}+03$ |  | 1.28E +00 | 1.50E-04 | $317 E-04$ | 1.28E401 | 278E-94 | 4 Ste.0s | 2 21E-0s | 3.06E.00 | 2 CzEOT | $3.40 E+09$ | C $07 E+08$ |
| $1.50 \mathrm{E}+00$ | 2,04E+04 | -250E+04 | $2315+03$ | 2 OEFOS |  | $1.54 \mathrm{E}+03$ | 1.40E-04 | 2 67E-OA |  | $2.74 \mathrm{E}-04$ | $451 \mathrm{E}-06$ | 274E-05 | $4.52 \mathrm{c}-\infty$ | $3.17 E-09$ | 3.60E +03 | 8 cextos |
| $1.26 \mathrm{E}+\infty$ | 2.335404 | 3.00E+04 | $2.04 \mathrm{E}+03$ | 3.40E +03 |  | $1.67 E+09$ | 1.24E-N | $2.28 E-04$ | $793 \mathrm{E}+\infty$ | $2006-04$ | 4.15E-08 | 3 40E-08 | $824 .-8$ | 3 SSE-OY | $363 E+\infty$ | $5806+02$ |
| $\begin{aligned} & 100 \mathrm{E}+00 \\ & \mathbf{7 . 0 6 E - 0 1} \end{aligned}$ | $2.70 E+04$ $300 E+04$ | -3.44E+04 | $307 E+03$ $340 E+03$ | $391 \mathrm{E}+03$ $452 E+03$ |  | $229 E+03$ $272 \mathrm{~F}+00$ | $112 \mathrm{C}-04$ 8.78 Cos | $180 E-O 4$ $1028-04$ | B 30E $+\infty$ $8006+\infty$ | 2 20EPO4 | ${ }^{4} 100 \mathrm{E} .06$ | 4.18E-05 | P49E-06 | 3 CeE M | $371 E+\infty$ 3 | ${ }^{6} 717+\infty$ |
| - 32E-01 | 3.56E+04 | - 5 SSE+04 | $4.04 \mathrm{E}+03$ | $816 E+03$ |  | $3.28 E+00$ | 8.77E-05 | 1.30E | 300 E |  | 3 80E-06 3 S0E-05 | 8.10E-08 43E-05 | 7.70¢-08 | $417 E-01$ 602009 | $377 E+03$ 3 S4E | $6 \operatorname{CaE}+62$ $\operatorname{CoE}+\infty$ |
| $502 \mathrm{E}-01$ | $407 \mathrm{E}+\mathrm{O} 4$ | 5 23E+04 | $481 \mathrm{E}+\infty 3$ | $893 E+03$ |  | $384 \mathrm{E}+03$ | 700 E .05 | 1.19E-04 | 3 16E $+\infty$ | 2.50e-04 | 3 31E-0 | 7 PEE-S | 1.10Eか5 | 8086501 | 3, 3.01E +03 |  |
| 3 90E-M | 4 E0E +04 | -506E+04 | $532 \mathrm{E}+03$ | 678 E 03 |  | $455 E+\infty$ | 6 ese-0s | $1.02 \mathrm{E}-04$ | 251E+C0 | 2.46E.O4 | 3 EsE-0s | ${ }^{8} 82 \mathrm{E}-08$ | 1.40e-0s | © 32 E -91 |  | +02 |
| $3.17 \mathrm{E}-91$ | 5.43E+04 | -68E+04 | $815 \mathrm{E}+03$ | $787 E+03$ |  | $538 E+03$ | -13E-05 | : 74E-08 | 1.09E $5 \times 0$ | $2305-94$ | 3 95E.05 | $1206-04$ | 1 1se-cs | $7006-01$ | 4.00E +03 | THE +02 |
| 2 52E-01 | $530 \mathrm{E}+\mathrm{O}$ | . 7 05E+04 | $714 \mathrm{E}+03$ | $8885+03$ |  | $637 \mathrm{E}+08$ | 850 C - | 7 49E-05 | 1 SEE+00 | $2.34 \mathrm{E} \cdot \mathrm{P} 4$ | 412 E .08 | 1.40E-04 | $2005-95$ | 705601 | $415 E+03$ | $7308+02$ |
| $200 \mathrm{E}-01$ | 7 24EE04 | -878EC04 | 321 E03 | 9 91E+03 |  | 744 t 03 | 4 23E-05 | - 45E-C6 | $1.25 E+\infty$ | 2 28E-04 | 400E.05 | 1 BiEEO4 | 3256.06 | 1808.01 | $4256+03$ | $7 \mathrm{CzE}+02$ |
| $1.50 \mathrm{E}-01$ | $822 \mathrm{E}+4$ | -91E+04 | $932 \mathrm{E}+03$ | $1.12 \mathrm{E}+04$ |  | \% 56E 03 | $4296-\infty$ | 5 C4E-03 | - 90E-01 | 2 20E-04 | 4.11E-0 | 2 206-04 | $412 \mathrm{E}-05$ | $1006+\infty$ | 140c+00 | $1235+02$ |
| 1.286 -09 | - $34 \mathrm{E}+04$ | $-1.12 \mathrm{E}+05$ | $1.085+04$ | $127 \mathrm{E}+04$ |  | $982 \mathrm{E}+03$ | ${ }^{381 E-05}$ | 4 93E-03 | 7 P3E-01 | $211 \mathrm{E}-04$ | 4 30E-C5 | 2 00E-04 | 883 Cos | $112 \mathrm{E}+00$ | 4 SSE +03 | 1 45E-02 |
| 1 OOE-01 | $100 \mathrm{E}+05$ | $-1.23 \mathrm{E}+\infty$ | $1.23 \mathrm{E}+04$ | $1.30 \mathrm{E}+04$ |  | 1 18Etor | 3 52E-¢ | 4 23E-05 | 2sed | 20 E-OA | 4 SOE-OS | 3.25E |  | 285 |  |  |



 $706 \mathrm{E}+027.17 \mathrm{E}+03 \mathrm{-1.14E+02} \mathrm{~B}$ 13E+02 $\quad 129 \mathrm{E}+01$ $632 \mathrm{E}+027.20 \mathrm{E}+03-2.46 \mathrm{E}+02 \mathrm{~B}$ 16E $102 \quad 279 \mathrm{E}+01$ $502 E+02$ 7.23E+03 $-3.14 E+02 \quad 20 E+02 \quad 356 E+01$ $\begin{array}{ccccc}3.99 E+02 & 727 E+03 & -3 & 87 E+02 & 625 E+02 \\ 3.30 E+01 \\ 3.17 E+02 & 7.32 E+03 & -465 E+02 & 8 & 30 E+02\end{array}$
 $2.00 E+027.43 E+03 \quad-6.52 E+02 \quad 8.42 E+02 \quad 7.30 E+01$ 1.50EE $027.7 .49 E+03-7.03 E+02840 E+02,06 E+01$
 1.00E+02 7.64E+03 -1.08E+03 B67E+02
 8.02E+01:03E+09 -1.7SE+03: I1E +02 3. $.00 \mathrm{E}+01$ 1 $16 \mathrm{E}+03 \mathrm{O}$-201E+03 $9.25 \mathrm{E}+02$ $\begin{array}{llll}3.17 E+01 & 1.3 E E+03 & -2.35 E+00 & 9.40 E+\infty 2\end{array}$ 2.52E+01 C OEE+03 $-2.76 E+033^{9} 76 E+02$







 $2.00 E+001$ 100E+04 $-9.94 E+032.16 E+03 \quad 1.13 E+03$ $4.59 E+00207 \mathrm{E}+04$-1.005+04 2 2SE $28 E+\infty 0225 E+04$ $1.00 E+00242 E+04-105 E+\infty 4274 E+03$ i.19E
 32E-01 $276 E+04,1.04 E+04313 E+03 \quad 1.18 E+03$ O2EE01 2.01E+04 -1 OOE +043 30E+03 $1.10 E+03$

 $200 E-013$ SOE $+04-1.00 E+041.97 E+031.21 E+00$
 $\begin{array}{llllll}1.28 E-01 & 382 E+04 & -1.16 E+04 & 4.33 E+09 & 1.32 E+01 \\ 100 E-01 & 3.98 E+04 & -1.19 E+04 & 4.49 E+03 & 1.35 E+03\end{array}$

 $300 E+002$ IEEE 7 TOTE-02 $704 \mathrm{E}+\infty$ : $52 \mathrm{E}-03 \mathrm{O} 3 \mathrm{STE}-\infty$ $1.12 \mathrm{E}+01802 \mathrm{E}-\infty 3250 \mathrm{E}-\infty$ $158 E+01$ 7.28E-05 $2.01 E-\infty$ $\begin{array}{llll}200 E+01 & 647 E-09 & 1.44 E-02 \\ 206 E+01 & 5.73 E-00 & 13 S E-02\end{array}$ $\begin{array}{llll}266 E+01 & 5.73 E-00 & 13 S E-02 \\ 3.29 E+01 & 5.03 E-03 & 1.13 E-02\end{array}$ $401 E+01441 \mathrm{E}-\infty \mathrm{S}$ O SIE-0 $401 E+9$ S. $78 E-\infty$ SOEDS $s$ TE+01 $3.27 E-\infty$ © 7 TRE-D
 $\begin{array}{lll}1.10 E 401 & 2.41 E-03 & 100 E-03 \\ 02 E+02 & 205 E-00 & 300 E-00\end{array}$
 $\begin{array}{lll}1.17 E+\infty & 1.7 E-\infty & 300 E-\infty \\ 130 E+\infty & 1.63 E-\infty & 2.06 E-\infty\end{array}$ $107 E+\infty$ $201 \mathrm{E}+\infty 2 \mathrm{I}$ 1.14E-03 $2.10 \mathrm{E}-\infty$


 $540 \mathrm{E}+02 \mathrm{~B}$ 30E-04 BeoE-O4 T2E 202 B7EE-O4 7.25E-O4

 1.3SE+03 4.37E-O4 3 OEEEOA ISAE + $1.74 E+\infty) 393 E-04207 E-O 4$ $185 E+003$ 3.75E-04 $2.31 E-04$ $\begin{array}{lll}213 E+\infty 0 & 3.57 E-04 & 201 E-04 \\ 232 E+\infty & \text { S } 43 E-04 & 174 E-04\end{array}$
 $\begin{array}{llll}208 E+08 & 315 E-O A & 133 E-04 \\ 283 E+000 & 300 E-04 & 127 E-O A\end{array}$ $208 E+03$ 2.00E-OA $118 E-04$ $\begin{array}{llll}3.16 E+03 & 2.76 E-O 4 & 100 E-04 \\ 335 E+00 & 203 E-04 & 7 S E-05\end{array}$



| quency | 2 | z' | $21 / \mathrm{cm}^{2}$ | $\mathrm{Z} / \mathrm{cm}^{2}$ | Re | Z'Rs | $r$ | ${ }^{\prime \prime}$ |  |  |  | rio | Y/w |  |  | 1/0c(s) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $200 \mathrm{E}+3$ | $681 \mathrm{E}+03$ | 2.75 | 773E+02 | -311E+01 | $R_{*}$ | -200E+00 | 2 ®7E | 16E- | $126 \mathrm{E}+04$ | $337 E-03$ | 2 63E-03 | 2 6sE-07 | 2 10E-07 |  | -1.84E+02 | C-02 |
| $159 E+03$ | 8 82E+03 | $163 E+02$ | 77 | -1 85E+01 |  | $-212 \mathrm{E}+\infty$ | +09E- | \$ 32E-02 | $98 \mathrm{E}+0$ | -7 10E-0 | $\cdot 105 E$ | -7.11E- | -1 05E-08 | .02E-03 | 40 | S3E+09 |
| $128 \mathrm{E}+03$ | $883 \mathrm{E}+03$ | $677 E+01$ | $7.75 \mathrm{E}+02$ | . $780 \mathrm{E}+00$ |  | $-104 E+00$ | -173E-20 | -128E-01 | 7 93E | $\rightarrow$ e6e- | -175E | - 62 E | -2 21E-03 | $112 \mathrm{E}-0$ | , 14 | 46E+00 |
| $100 \mathrm{E}+03$ | 6 84E+03 | -2.35E+01 | $776 E+02$ | $288 \mathrm{E}+00$ |  | $4895-01$ | $686 E-02$ | $363 \mathrm{E}-01$ | ${ }^{3} 30 \mathrm{E}$ | - $43 \mathrm{E}-0$ | 241 E | 5 44E | -s 82E-05 | $120 \mathrm{E}-02$ | - | $107 E+\infty$ |
| 7 96E+02 | $888 \mathrm{E}+03$ | $-109 E+02$ | $778 E+02$ | 1.24E |  | $238 \mathrm{E}+\infty 0$ | 149E-02 | 7.77E-02 | 500 E -03 | - 59 | 2 SeE-02 | 1 72E-07 | -5 18E-06 | $141 \mathrm{E}-02$ | 128 | $\checkmark$ asexal |
| $632 \mathrm{E}+02$ | $689 \mathrm{E}+03$ | -1 88E+02 | 7.81E+02 | $213 \mathrm{E}+09$ |  | 5 46E+00 | 1 13E-02 | $440 \mathrm{E}-02$ | $397 \mathrm{E}+03$ | 148 E | 1.11E-02 | 3 72E-07 | -2 80E-06 | $1.59 \mathrm{E}-2$ | 1.17 | - $33 \mathrm{E}+01$ |
| $502 \mathrm{E}+02$ | $681 \mathrm{E}+03$ | $280 \mathrm{E}+02$ | 7 84E+02 | $317 \mathrm{E}+01$ |  | $8.29 \mathrm{E}+00$ | 7.71E-03 | 2 05E-02 | 3.16E+03 | 186 E - | $601 \mathrm{E}-03$ | 5 C9E-07 | -1 OOE-0 | $1.78 \mathrm{E}-02$ | $471 E$ | -1 52E+02 |
| $399 \mathrm{E}+02$ | $894 \mathrm{E}+03$ | S.78E+02 | 7.87E+02 | $428 \mathrm{E}+01$ |  | 1.15E+01 | $587 \mathrm{E}-03$ | 2.18E-02 | $251 E+03$ | 188 E | -3 67E-03 | $748 \mathrm{E}-07$ | 1.47E-06 | $200 \mathrm{E}-02$ | 1.10 | -2 16E402 |
| $317 \mathrm{E}+02$ | 6 99E+03 | 4 98E +02 | $792 \mathrm{E}+02$ | $565 E+01$ |  | 1.67E+01 | $481 \mathrm{E}-03$ | 1 63E.02 | 1.99E+03 | 1.71E-03 | -1 84E-03 | 8 80E-07 | +24E-07 | 2 24E-02 | 27 | -2 01E+02 |
| 2 52E+02 | $703 \mathrm{E}+03$ | - 32E+02 | 7.97E+02 | $7.17 \mathrm{E}+01$ |  | $218 E+01$ | $388 \mathrm{E}-03$ | 1.28E-02 | $158 \mathrm{E}+03$ | 1 CSE.03 | - 46E-04 | 1.04E | -608E-07 | $251 \mathrm{E}-02$ | 4 S0E+02 | -2 1 1E+02 |
| $2.00 \mathrm{E}+02$ | $709 \mathrm{E}+03$ | . 7 74E+02 | : $04 \mathrm{E}+02$ | $8{ }^{1} 7 \mathrm{E}+01$ |  | $2.78 \mathrm{E}+01$ | 3 29E-03 | 104E-02 | 1.26E+03 | $144 E .03$ | - $07 \mathrm{E}-04$ | $114 \mathrm{E}-\mathrm{C}$ | - $403 \mathrm{E}-07$ | $282 \mathrm{E}-02$ | -10E+02 | -2 18E+02 |
| $159 \mathrm{E}+02$ | 7.15E+03 | $\rightarrow 42 \mathrm{E}+02$ | $810 \mathrm{E}+02$ | $107 \mathrm{E}+02$ |  | $347 \mathrm{E}+01$ | $275 E-03$ | $847 \mathrm{E}-03$ | $\bigcirc 96 E+02$ | 1.32E-OS | $228 \mathrm{E}-04$ | 1 32E-0 | -2 28E-07 | $317 \mathrm{E}-02$ | 7.30E+02 | -1.27E+02 |
| $1.26 \mathrm{E}+02$ | $7.22 \mathrm{E}+03$ | -1.13E+03 | $19 \mathrm{E}+02$ | $1.29 \mathrm{E}+02$ |  | $432 \mathrm{E}+01$ | 2 35E-03 | 6 89E-03 | $793 \mathrm{E}+02$ | $114 \mathrm{E}-03$ | -5 81E-05 | 143 E | . 7 33E-08 | 3 S5E-02 | 77E02 | 40E+01 |
| $100 \mathrm{E}+02$ | $731 \mathrm{E}+03$ | -1.36E+03 | $829 \mathrm{E}+02$ | $1.55 \mathrm{E}+02$ |  | $536 E+01$ | $201 \mathrm{E}-03$ | $5.77 \mathrm{E}-03$ | 6.30E+02 | 1 00E-03 | 9 Ope-05 | 1 S0E | $144 \mathrm{E}-07$ | 3 90E-02 | - 8EE+02 | CeSE+01 |
| 7 96E+01 | $742 \mathrm{E}+03$ | $-183 \mathrm{E}+03$ | 8.42E+02 | ${ }^{185 E+02}$ |  | $659 \mathrm{E}+01$ | 1.71E-03 | $480 \mathrm{E}-03$ | $500 \mathrm{E}+02$ | 8 $78 \mathrm{E}-04$ | 1.54E-04 | 1.75E-06 | $308 E-07$ | 4.47E-02 | ; 11 Et03 | 1 OSE+02 |
| ${ }^{6} 32 \mathrm{SE+01}$ | $7.55 \mathrm{E}+03$ | -1 95E+03 | S6E+02 | 221E+02 |  | -06E+01 | 1.45E-03 | 3 99E-03 | $397 \mathrm{E}+02$ | $7.77 \mathrm{E}-04$ | 2.12E-04 | 1.96E-08 | $833 \mathrm{E}-07$ | $802 \mathrm{E}-2$ | 1.20E+03 | 3.20E+02 |
| $502 \mathrm{E}+01$ | 7 89E+03 | $-238 E+03$ | : $72 \mathrm{E}+02$ | 2.70E+02 |  | 964 E 01 | $117 \mathrm{E}-03$ |  | $318 E+02$ | 8.16E-04 | 1 93E-04 | 2 SPE-D | -12E-07 | 8 63E-02 | i. $16 \mathrm{E}+03$ | $275 E+02$ |
| $309 \mathrm{E}+01$ | 7.89E+03 | - $277 \mathrm{E}+03$ | 8 P5E+02 | $315 E+02$ $375 E+02$ |  | $119 E+02$ | 1 05E-03 | $278 E-03$ | $251 \mathrm{E}+02$ | 6 OME-04 | $2.43 E-04$ | $241 \mathrm{E}-08$ | -69E-07 | ${ }_{6} 32 \mathrm{EE-02}$ | 1.42E 203 | $372 E+02$ |
| 3.17E+01 <br> $252 \mathrm{E}+01$ | 8.13E+03 8.40E+03 | $-3.31 \mathrm{E}+03$ <br> -304 t | $921 \mathrm{E}+02$ $053 \mathrm{E}+02$ | $3.75 E+02$ $447 E+02$ |  | 1.48E+02 | 8 90E-04 | $2.32 \mathrm{E}-03$ $1.03 \mathrm{E}-03$ | 1 99E+02 | $532 \mathrm{E}-04$ $474 \mathrm{E}-04$ | $248 \mathrm{E}-04$ | $287 \mathrm{E}-08$ 3006 | 1.23E-06 | 7.00E-02 | 1.5sE+03 | $717 E+02$ |
| $2.00 \mathrm{E}+01$ | 75E+03 | - 4 69E+03 | 9 92E+02 | $532 \mathrm{E}+02$ |  | 1.77E+02 | $706 E-04$ $857 E-04$ | 1.03E-03 $101 \mathrm{E}-03$ | 158 | 4.74 | 2 35E | 3.00E-08 | 1498.06 | 7 05E-02 | 1.89E+03 | 10E+02 |
| $159 \mathrm{E}+01$ | 9.18E+03 | -5 57E+03 | 1.04E+03 | $832 \mathrm{E}+02$ |  | $2.65 \mathrm{E}+02$ | 5 CAE-O4 | 1.35E-03 | O98E+01 | $424 \mathrm{E}-04$ $383 \mathrm{E}-04$ |  | 337 E | 1.73E | 192E-02 | 1.87 |  |
| 1.28E+01 | $970 \mathrm{E}+03$ | -59E+03 | 1.10E+03 | $748 \mathrm{E}+02$ |  | $3.24 \mathrm{E}+02$ | $488 \mathrm{E}-04$ | 1.13E-03 | 7.93E+01 | 9.50 | 1.73E | 4.41E-06 | 2.18E-08 | $1.12 \mathrm{E}-01$ | $2 \mathrm{COE}+03$ |  |
| $1.00 \mathrm{E}+$ | 1.03E+0 | -7.78E+03 | 4.17E+03 | $182 \mathrm{E}+02$ |  | $3.96 \mathrm{E}+02$ | 4 23E-04 | - 44E-04 | 6.30E+01 | 3.25E-04 | 1.48E-04 | 5.16E-00 | $234 \mathrm{E}-08$ | .28E-09 | 2 55E+03 | $1.16 E+03$ |
| $7.96 \mathrm{E}+0$ | 1.11E | -9.16E+03 | $1.26 E+03$ | 1 OAE+03 |  | $4.84 \mathrm{E}+02$ | 5 69E-04 | 7.91E-04 | 5 00E+01 | 3 00E-O4 | 1.26E-04 | 6.12E-08 | 2.51E-00 | 41E-01 | $2.60 \mathrm{E}^{\text {co3 }}$ | 3 |
| $632 \mathrm{E}+00$ | 121E+0 | -1.08E+04 | 1.37E+03 | 1.22E+03 |  | $59 \mathrm{ME}+02$ | $322 \mathrm{E}-04$ | 8 63E-04 | $397 E+01$ | 2 92E-04 | 1.00E-04 | 7.38E-06 | 271 E-0 | 1.99E-01 | $301 E+03$ | l.11E-03 |
| $5.02 \mathrm{E}+00$ | 1.32E+0 | -1.28E+04 | 1.50E+03 | $1.42 E+03$ |  | 7.22E+02 | $283 \mathrm{E}-04$ | 5.59E-04 | $316 \mathrm{E}+01$ | $201 \mathrm{E}-04$ | - 08E-05 | 192E-08 | 2 87E-00 | 1.78E-01 | 3.22E+03 | I.04E+03 |
| 3 99E+00 | $146 \mathrm{E}+0$ | -1.48E+0 | 1 65E+03 | 1 88E+03 |  | $4.78 E+02$ | 2 49E-04 | 4.71E-04 | 251 E 01 | $2.73 \mathrm{E}-04$ | $780 \mathrm{E}-05$ | 1.09E-05 | 3.11E-00 | $2006-01$ | j 36E+03 | - $55 \mathrm{E}+02$ |
| $317 \mathrm{E}+00$ | $1.62 \mathrm{E}+0$ | -1.70E | 1.84E+03 | $193 E+03$ |  | 1.06E+03 | $219 \mathrm{E}-04$ | 3 08E-04 | $199 \mathrm{E}+01$ | 2 67E-04 | 6 65E-05 | 1.34E-05 | 3 34E-06 | 2 24E-01 | 3 33E+03 | 02 |
| 2.52E+00 | 1.81E+04 | -1.96E+04 | $205 E+03$ | 2.23E+03 |  | 1.20E+03 | $194 \mathrm{E}-04$ | 3 36EE-04 | 1.58E+01 | $281 \mathrm{E}-04$ | 5 cee-05 | 1 85E-05 | 3 58E-00 | $251 \mathrm{E}-01$ | ; 6eEf03 | $782 \mathrm{E}+02$ |
| 2 OOE +00 | 1.91E+0 | 2.18E+04 | $2.18 \mathrm{E}+03$ | $245 E+03$ |  | 1.39E+03 | 1.75E-04 | 3.09E-04 | $126 E+01$ | 2 S4E-O4 | $2896-05$ | $2.02 \mathrm{E}-05$ | 2.30E-08 | $2.62 E-01$ | ; $09 \mathrm{E}+03$ | ${ }^{1} 44 E+02$ |
| $159 \mathrm{E}+00$ | $227 \mathrm{E}+04$ | -2 59E+04 | $250 E+03$ | $294 \mathrm{E}+03$ |  | $1.80 \mathrm{E}+03$ | 1 52E-04 | $2.47 \mathrm{E}-04$ | 9 98E+00 | 2 53E-04 | 4 21E-0S | $2.54 \mathrm{E}-03$ | $422 \mathrm{E}-06$ | 3.17E-01 | S.MUE+03 | 30E +02 |
| 1.28E +00 | $255 \mathrm{E}+04$ | -2 28 E +04 | 2 90E+03 | 3 38E +03 |  | $2.12 \mathrm{E}+03$ | 1.33E-04 | $212 \mathrm{E}-04$ | 7 93E+00 | $251 \mathrm{E}-04$ | 3 AME-0S | $317 \mathrm{E}-05$ | 4 ESE-9 | $3 \mathrm{SSE-01}$ | 3 CPE +03 | 5 C0E-02 |
| $1.006+00$ | 2 99E+04 | $-3.27 E+04$ | 3 40E+03 | $371 E+03$ |  | $2.62 \mathrm{E}+03$ | 1.27E-04 | 1.00e-04 | $830 \mathrm{E}+00$ | $2.38 \mathrm{E}-04$ | $382 \mathrm{E}-05$ | 3.77E-03 | - 07E-06 | 3 PeE-01 | $4.10 \mathrm{E}+03$ | - $00 \mathrm{E}+02$ |
| 7.96E-01 6 32E.01 | $334 \mathrm{E}+04$ | -3 88E+04 | $378 \mathrm{E}+03$ | $438 E+03$ |  | $3016+03$ | 1.07E-04 | 1.55E-04 | 5 00E+00 | $241 \mathrm{E}-04$ | $358 \mathrm{E}-55$ | 482E-05 | 7.17E-08 | $447 E-01$ | 4 O5E +09 | ${ }^{0} 02 \mathrm{E}+02$ |
| $\begin{aligned} & 632 \mathrm{E}-01 \\ & \mathbf{S . 0 2 \mathrm { E } - 0 1} \end{aligned}$ | 383E+04 | ${ }_{-}^{4.38 E+04}$ | $434 \mathrm{E}+03$ | 494 E 03 |  | $357 \mathrm{E}+03$ | 2 80E-05 | $133 \mathrm{E}-04$ | 3.97E +00 | 2 38E-04 | 3.40E-05 | 8 00E-05 | 4.71E-08 | $502 \mathrm{E}-1$ | 4.12E+03 | C1E+02 |
| 5.02E-01 | 4 41E+0 4 98E+0 | -602E04 | 5 O0E +03 | $570 E+03$ |  | $4.22 \mathrm{E}+03$ | 8 400-05 | 1.13E-04 | 3.18E+00 | $233 \mathrm{E}-04$ | $373 E-05$ | 7.37E-0S | 1.18E-0S | 5 E3E-01 | 4.10E 03 | C 73E+02 |
| 3 99E-01 3 17E-01 | $498 E+0$ $561 E+0$ | $-564 \mathrm{E}+04$ $-38 \mathrm{E}+04$ | 5 65E-03 | 640E+03 |  | ${ }^{4} 878 \mathrm{E}+03$ | $753 \mathrm{E}-05$ | 9 90E-05 | $251 \mathrm{E}+00$ | $230 \mathrm{E}-04$ | 3 53E-05 | - 15E-03 | 1.41E-05 | - 32E-01 | $4206+03$ | 6 SSE+02 |
| $317 E-01$ | $561 E+0$ | -38E+04 | 636 E 03 | $7.23 E+03$ |  | 5 58E+03 | 6 80E-05 | 8 67E-05 | 1.09E+00 | 2 22E-04 | S $686-05$ | 1.12E.04 | 1 94E.0S | 7.00E-01 | $438 E+03$ | $721 E+02$ |
| 2 52E-09 | $\mathrm{S}_{4} 4 \mathrm{E}+0$ | . 7 15E+04 | 7 25E+03 | 8.11E+03 |  | $6.48 \mathrm{E}+03$ | $601 \mathrm{E}-05$ | 7.53E-05 | 1.58E + | $218 \mathrm{E}-04$ | 3.83E.05 | 1.38E-04 | $242 \mathrm{E}-05$ | 7.958 .01 | $445 E+03$ | 7 33E+02 |
| 2 20E-01 | 7 30E+09 | - O9E+04 | 28E403 | - $17 \mathrm{~F}+03$ |  | $7.50 E+03$ | $534 \mathrm{E}-05$ | 8 53E-05 | $1.28 E+00$ | 2.12E-04 | 3 CoE-05 | 1.00E-94 | 3.11E-05 | S $02 \mathrm{E}-01$ | $450 \mathrm{E}+03$ | ( $30 \mathrm{E}+02$ |
| 1.59 E .01 | B4E +0 | $\rightarrow .16 \mathrm{E}+04$ | 9 53E-03 | 1 104E+04 |  | $175 \mathrm{E}+0 \mathrm{~S}$ | $474 \mathrm{E}-05$ | 5 83E-05 | - $28 \mathrm{E}-01$ | 2 OLE-04 | $411 \mathrm{E}-05$ | 2.04E-04 | $412 \mathrm{E}-05$ | $100 \mathrm{E}+00$ | 4 72E+03 | 63E+02 |
| 1.28E-01 | 9 45E+04 | -1.05E+05 | $107 \mathrm{E}+04$ | $119 E+04$ |  | 9 94E+03 | 4.16E-05 | 4 05E-05 | 7 93E-01 | 1.88E-04 | 431 E .05 | 2 40E-04 | 8.44E-05 | 1.12E+00 | 4 13E+03 | $105 E+03$ |
| 1.00 E | 1.06 E | -1.19E+05 | $1.20 \mathrm{E}+04$ | $134 \mathrm{E}+04$ |  | 1.13E+04 | $366 E-05$ | 437 E .05 | $826 E-01$ | 1.00E-04 | $437 \mathrm{E}-5$ | $302 \mathrm{E}-04$ | 6 DSE-OS | 1. $28 \mathrm{E}+00$ | S OOE +03 | $115 E+03$ |

$\begin{array}{llllllllllll}200 E+03 & 7.12 E+03 & 248 E+02 & 8.00 E+02 & -201 E+01 & 8.13 E+02 & -518 E+00-34 E-03-34 E-02 \\ 159 E+03 & 7.14 E+03 & 1.33 E+02: 10 E+02 & -150+01\end{array}$


 $632 \mathrm{E}+027.26 \mathrm{E}+03-293 \mathrm{E}+02 \mathrm{a} \quad 23 \mathrm{E}+02 \quad 264 \mathrm{E}+01$
 $309 E+027.35 \mathrm{E}+03-4.12 \mathrm{E}+028.33 \mathrm{E}+02 \quad 4.67 \mathrm{E}+01$ $\begin{array}{lllll}3.17 E+02 & 7.40 E+03 & -5.07 E+02 & 8.39 E+02 & 575 E+01 \\ 2.52 E+02 & 7.46 E+03 & -12 E+02 & 8.45 E+02 & 894 \mathrm{E}+01\end{array}$
 $1.59 E+027.59 E+03 \rightarrow 60 E+02861 E+02 \quad 976 E+01$ $\begin{array}{ll}1.20 \mathrm{E}+02 & 7.68 \mathrm{E}+03-1.02 \mathrm{E}+03 \\ \mathbf{1} .71 \mathrm{E}+02 & 1.15 \mathrm{E}+02\end{array}$ $1.00 E+027.75 E+03-1.19 E+03: 82 E+02 \quad 1.35 E+02$ $\begin{array}{ccccc}\text { 7.06E }+01 & 7.00 E+03 & -1.40 E+03 & \text { a } 96 E+02 & 1.50 E+02 \\ 832 \mathrm{E}+01 & 804+03\end{array}$
 $3.00 \mathrm{E}+01$ e.40E+03-2.24E+03 $9.53 \mathrm{E}+022.54 \mathrm{E}+02$ 3 17E+01 $263 E+03-2.02 E+03$ 0.79E+02 $2.98 E+02$ .52E+01 $892 \mathrm{E}+03-307 \mathrm{OE}+03101 \mathrm{E}+03 \quad 3.48 \mathrm{E}+02$ 00E+01 $0.2 \mathrm{EEE}+03-3.57 E+03$ I.OSE+03 $405 \mathrm{E}+02$

 \begin{tabular}{lllll}
\& 205 \& $1.03 E+04$ \& $-480 E+03$ \& $1.16 E+03$ <br>
\hline

 $708 \mathrm{E}+00$ i.18E+04 $6.24 \mathrm{E}+03 \mathrm{~B}$ i.33E+03 $707 \mathrm{E}+02$ .32E+00 $1.28 E+04-6.09 E+03 \quad 1.45 \mathrm{E}+03 \quad 7.03 \mathrm{E}+02$ $3.02 \mathrm{E}+001.30 \mathrm{E}+04-7.74 \mathrm{E}+031.58 \mathrm{E}+03 \quad \mathbf{1 . 7 7 E}+02$ $1.96 \mathrm{E}+001.52 \mathrm{E}+04-6.43 \mathrm{E}+031.72 \mathrm{E}+03956 \mathrm{E}+02$ $\begin{array}{llll}3.17 E+00 & 1.67 E+04 & -006 E+03 & 1.69 E+03 \\ 1.03 E+03\end{array}$ 

$2.00 E+00$ \& $1.09 E+04$ \& $0.50 E+03$ \& $2.07 E+03$ \& $1.00 E+03$ <br>
\hline
\end{tabular} $1.59 \mathrm{E}+002.16 \mathrm{E}+04$-1.03E+04 $2.45 \mathrm{E}+03 \mathrm{i} 1.17 \mathrm{E}+03$ .26E+00 $233 E+04-1.05 E+04264 E+03119 E+03$ OOE $+00250 E+04-1.07 E+04283 E+03 \quad 1.21 E+03$ $7.98 \mathrm{E}-01268 \mathrm{E}+04-107 \mathrm{E}+043.02 \mathrm{E}+03 \quad 1.21 \mathrm{E}+03$

 $399 E-01 \quad 314 E+04-107 E+04,30 E+03 \quad 1.23 E+03$ 3.17E-01 3 30E +04 -1.10E+04 $3.74 \mathrm{E}+03 \mathrm{I}$ 1.25E+03 2.52E-01 3.43E+04 -1.11E+04 $390 \mathrm{E}+03 \quad 1.28 \mathrm{E}+03$ $200 \mathrm{E}-01350 \mathrm{~S}+04-1.13 \mathrm{E}+04407 \mathrm{E}+03$;28E+03 $1.59 E-01 \quad 3.77 \mathrm{E}+04-1.10 \mathrm{E}+041.28 \mathrm{E}+031.34 \mathrm{E}+03$ $\begin{array}{llll}1.20 E-01 & 3.02 E+04 & -1.24 E+04 & 4.45 E+03 \\ 1.00 E-01 & 1.41 E+03 \\ 4.10 E+04 & -1.31 E+04 & 4.65 E+03 & 1.40 E+03\end{array}$
$\begin{array}{ccc}538 E+00 & 158 E-02 & 8.18 E-02 \\ 1.02 E+01 & 1.20 E-02 & 320 E-02\end{array}$ $\begin{array}{lll}1.02 E & 40 \mathrm{E}+01 & 957 \mathrm{E}-03 \\ 235 E-02\end{array}$ $\begin{array}{lll}140 E+01 & 97 E E-03 & 235 E-02 \\ 2.00 E+01 & 7.75 E-03 & 1.01 E-02\end{array}$ $2.50 E+01$ © $52 \mathrm{E}-03 \mathrm{~S} 1.45 \mathrm{E}-02$ $\begin{array}{lll}\text { 25E+01 } & \$ 53 E-03 & 1.10 E-02 \\ 3.86 E+01 & 472 E-03 & 9.05 E-03\end{array}$ $461 \mathrm{E}+01$ 4.07E-03 $\mathrm{E} .25 \mathrm{E}-03$ 5.79E+01 $3.40 \mathrm{E}-03 \mathrm{~B} .93 \mathrm{E}-03$

 | $828 E+01$ | $258 E-03$ |
| :--- | :--- | :--- | $\begin{array}{lll}206 E+01 & 2.23 \mathrm{E}-03 & 4.20 \mathrm{E}-03\end{array}$

 $\begin{array}{lll}1.40 E E 02 & 1.06 E-03 & 3.02 E-03 \\ .06 E+02 & 1.43 \mathrm{E}-03 & 256 \mathrm{E}-03\end{array}$ $\begin{array}{llll}1.06 E+02 & 1.24 E-03 & 2.17 E-03 \\ & 905 & \end{array}$ $\begin{array}{llll}30 E+02 & 1.08 E-03 & 1.83 E-03\end{array}$ \begin{tabular}{lll}
$68 E+02$ \& $48 E-04$ \& $185 E-03$ <br>
\hline

 

$.51 E+02$ \& 1 \& 3 \& SE-04 <br>
\hline

 $\begin{array}{lll}27 E+02 & 7.48 \mathrm{E}-04 & 1.09 \mathrm{E}-03 \\ 21 \mathrm{E}+02 & \mathrm{~B} .75 \mathrm{E}-04 & 917 \mathrm{E}\end{array}$ $\begin{array}{lll}21 E+02 & \text { 6.7E-01 } & 917 E-04 \\ 33 E+02 & \text { O. } 15 E-04 & 7.70 E-04\end{array}$ 7.63E+02. 5.65E-04 $649 \mathrm{E}-04$ $10 E+02 \$ 22 E-04549 E-04$ .08E+03 4. $868 \mathrm{E}-04465 \mathrm{E}-04$ 

$28 E+03$ \& $45 E E-04$ <br>
\hline \& $94 E E-04$
\end{tabular} $\begin{array}{llll}.44 E+03 & 4.28 E-04 & 3.30 E-04 \\ 163 E+03 & 405 E-04 & 280 E-04\end{array}$

 202E+03 3 85E-04 $2.18 \mathrm{E}-04$ $21 \mathrm{E}+03 \mathrm{3} 48 \mathrm{E}-041.01 \mathrm{E}-04$ 39E +03 3 $34 E-04168 E-04$ 58E+03 $317 \mathrm{E}-041.51 \mathrm{E}-04$ $2.75 E+033$ OSE-O4 $134 \mathrm{E}-0$ $\begin{array}{llll}293 E+03 & 200 E-04 & 1.23 E-04 \\ & 08 E+03 & 278 E-04 & 14 E-04\end{array}$ | $108 E+03$ | $278 E-04$ | $1.14 E-04$ |
| :--- | :--- | :--- |
| $26 E+03$ | $206 E-04$ | $04 E-N$ | $\begin{array}{lll}1.26 E+03 & 260 E-04 & 104 E-0\end{array}$ $364 E+03239 E-04,28 E-05$ $384 \mathrm{E}+03$ 2.27E-04 $8.74 \mathrm{E}-05$





| frequency | Z | ${ }_{2 \times 10}$ | $\mathrm{z} / \mathrm{cm}^{2}$ | 2"/cm ${ }^{2}$ |  |  |  | $\mathbf{V}^{\mathbf{*}}$ |  |  | $r{ }^{\prime \prime}$ | r | Y'/ | (w) | ) | 1/uc(s) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 200E $+\infty 0$ | ¢03E+03 | $281 \mathrm{E}+\infty 2$ | $752 \mathrm{E}+02$ | -2 98E+01 | 7.56E+02 | -3.00E +0 | -75E03 | 34E-02 |  | DEE-D | $-435 E-0$ |  |  | -92e-03 | $\begin{gathered} (8) \\ -1 \text { 18E+0 } \end{gathered}$ | $-1.23 E+02$ |
| $1.50 \mathrm{E}+\infty$ | 4 C4E+03 | $152 \mathrm{E}+02$ | 7 73E+02 | -1.72E+01 |  | $-182 \mathrm{E}+00$ | - $078-93$ | -574E-02 | $\text { - SeE }+\infty$ | 4.24E-02 | $-206 E-02$ | - 1.24 E -06 | $\begin{aligned} & 3 \text { SUE-07 } \\ & \text {-2.0BE-00 } \end{aligned}$ | $\begin{aligned} & 982 E-03) \\ & 100 E-02 \end{aligned}$ | $-116 E+02$ $-1.44 E+01$ | - $1.23 \mathrm{E}+02$ -. $00 \mathrm{E}+01$ |
| $1.28 E+103$ | 5 OSE+03 | 6.00E+01 | 7 74E+02 | - $76 \mathrm{E}+\infty$ |  | - $78 E-91$ | 2 Sce-pa | -1 $706-01$ | 789 E | 1.70E-01 | 1.16E+00 |  |  | 100E-02 |  | 1.006t01 |
| $100 \mathrm{E}+\infty$ | - 08E+03 | -4 45E+01 | $756 E+02$ | $504 E+\infty$ |  | 6.73E-09 | 2 61E-02 | 1.95E-01 |  |  |  |  |  |  | 125E-01 | [41E-01 |
| 7.96E +02 | - $68 E+03$ | -1.36E+02 | 7.57E+02 | 1.54E+01 |  | $247 \mathrm{E}+\infty$ | $1.01 \mathrm{E}-02$ | \% 33E-02 | 8.00E +03 | $2.44 E-\infty$ | - 2.40 EE-02 | 4 BEE- | 191E-08 | $\begin{aligned} & 1.26 E-02 \\ & 1.41 E-00 \end{aligned}$ | 1.0 |  |
| -372 +02 | C.70E+03 | -196E+02 | 700 E 02 | $2.238+01$ |  | $4.77 E+\infty$ | \% 19E-03 | 4.29E-02 | 3.97E +13 | $105 E-03$ | -1 57E-02 |  | - 406 -08 |  | 4.0 |  |
| $502 \mathrm{E}+02$ | $173 E+03$ | 2. 15E+02 | $763 \mathrm{E}+02$ | $357 \mathrm{E}+01$ |  | 3 4E+00 | $627 \mathrm{E}-03$ | $2.05 E-02$ | $318 E+\infty$ | $203 \mathrm{E}-03$ | -1 7re-03 | C.44E-0 | 3.15E-08 | $1 \mathrm{SOE-02}$ | SOEE |  |
| $3906+02$ | 4.70E+03 | - $26 \mathrm{EE}+02$ | $7.67 \mathrm{E}+02$ | 4 83E+01 |  | 1 17E+01 | $474 \mathrm{E}-03$ | 1.98E-02 | $251 \mathrm{E}+\infty$ | 1.08 | $420 \mathrm{E}-03$ |  |  | $200 E-02$ | cos | -1 3SE+02 |
| $317 \mathrm{E}+02$ | © 80E+03 | -5 52E+02 | $774 \mathrm{E}+02$ | $528 \mathrm{E}+01$ |  | $1.61 \mathrm{E}+0 \mathrm{O}$ | 3 86E-03 | 1.50E-02 | $100 \mathrm{E}+\infty 3$ | 1 180E-03 | -2 67E-03 | $002 \mathrm{E}-0$ |  |  | 1 TBE+02 | -1 0 CEFCO2 |
| $2525+02$ | 6 85E+03 | -92E+02 | $778 E+\infty$ | 7 ESE +01 |  | $215 E+01$ | $325 E-03$ | 1.19E-02 | $1.58 \mathrm{E}+\infty 3$ | 1 57E-03 | -1.76E-03 | - $35 E-0$ | (1.11E-08 | $2.24 E-02$ $281 \mathrm{E}-02$ | $173 E+02$ | $-258 E+02$ $-16 E+00$ |
| $200 \mathrm{E}+02$ | $680 \mathrm{E}+00$ | -31E+02 | $782 \mathrm{E}+02$ | - 42E+01 |  | $208 E+01$ | $2.77 \mathrm{E}-03$ | $983 \mathrm{E}-03$ | $1.268+\infty$ | 1.38E-08 | -1.45E-03 | 1.10E | 1.15E-08 |  |  |  |
| $1.506+02$ | 8 95E +03 | - 88E+02 | $7.88 \mathrm{E}+02$ | 112E+02 |  | 3 30E401 | 2.42E-03 | 5 21E-03 | 9.98E+02 | 115 E - |  | 1.16E- | -1.15E-06 |  |  |  |
| 1.28E+02 | 7.03E+03 | -1.206+03 | $797 \mathrm{E}+02$ | 1.38E+02 |  | $418 \mathrm{E}+01$ | 2.08E-03 | 8 70E-03 | $703 \mathrm{E}+02$ | $102 \mathrm{E}-03$ | -7.45E-04 | 1.29E- | -1.15E-06 | $317 E-02$ $3.5 S E-\infty$ | - 3 SEF+02 |  |
| $1.006+02$ | $712 \mathrm{E}+03$ | -1 46E+03 | $108 \mathrm{E}+02$ | 1 05E+02 |  | $528 \mathrm{E}+01$ | 1.76E-03 | 5 50E-03 | $630 \mathrm{E}+\infty 2$ |  | -4.50E-04 | 1.44 E - | 7.20E-07 | 3.56E-02 | - $78 E+02$ |  |
| 7 PeE+01 | 7.28E+03 | -1 $838+03$ | - 25E+02 | 2.07E+02 |  | 701 E +01 | 1 $45 E-03$ | $433 \mathrm{E}-03$ | $500 \mathrm{E}+02$ | $133 \mathrm{E}-04$ | - 5 00e-0 | $1.64 \mathrm{E}-0$ | -7.29E-07 | $3.60 E-02$ $447 E-02$ | 1.76E |  |
| $632 \mathrm{E}+01$ | $743 \mathrm{E}+03$ | -2.19E+03 | $142 \mathrm{E}+02$ | 2.49E+02 |  | - 72E+01 | $12 \mathrm{EE-03}$ | 3 5eE-03 | 3 97E+02 |  | $538 \mathrm{E}-\infty 5$ | 1 1 3 1 |  |  | 1.18 | $1006+01$ |
| $5028+01$ | $758 E+03$ | -2 $\mathbf{8 5 E}+103$ | $857 \mathrm{E}+02$ | $3.006+02$ |  | $102 \mathrm{E}+02$ | $102 \mathrm{E}-03$ | 2.88E-09 | 3.16E+02 | 7.23E-04 | 1.38E-04 | 197E-08 | $1.3 E E-7$ $430 E-97$ |  | ${ }_{1} 1.37 E+03$ | 100E $+\infty 2$ |
| $3006+01$ | $784 \mathrm{E}+03$ | - $3.13 \mathrm{E}+03$ | 80E +02 | 3.56E+ |  | $134 \mathrm{E}+02$ | - 30E-94 | $247 \mathrm{E}-03$ | $251 E+02$ |  |  |  |  |  | 1 | $1,41 E+02$ $4.74 E+08$ |
| $3175+01$ | $5115+03$ | -3.72E+03 | -20E+02 | $422 E+02$ |  | $105 \mathrm{E}+02$ | $804 E-04$ | $2056-03$ | 10E+02 | 4 TSE-O4 | ${ }^{1} 1786 E-04$ | $220 E-\infty$ $2.306-08$ |  | $\begin{aligned} & 632 x \\ & 700 \end{aligned}$ | 18 | 4.74E+02 |
| $2.52 z+01$ | $148 \pm+03$ | - -. $42 \mathrm{E}+03$ | $9509+02$ | 801 E 802 |  | $2.04 \mathrm{E}+02$ | 6 97E-04 | $171 \mathrm{E}-03$ | $158 \mathrm{E}+02$ | $414 \mathrm{E}-04$ | 1.73E-O4 | 262E-0 | 1.00E-08 | $7006-02$ | $188 E+\infty$ $208 E+\infty 3$ | C72E602 |
| $2.006+01$ | 0 C8E+03 | $524 \mathrm{E}+03$ | $1.01 \mathrm{E}+03$ | 5.94E+02 |  | $252 \mathrm{C}+02$ | COEE-O4 | 1.43E-03 | 1.28 | 3 enE-04 | 1706 -0 | 2 00E-08 | 1.35E-08 |  |  |  |
| $150 \mathrm{E}+\mathrm{C}$ | $\square^{40 E+03}$ | -18E+03 | 1.07E+03 | $7.01 \mathrm{E}+02$ |  | $3.11 \mathrm{E}+02$ | $52 \mathrm{EE}-04$ | 1.19E-03 |  | $324 \mathrm{E}-04$ | 1 sek-o4 | $325 E-\infty$ | 1.5EE-08 | 100801 | $2208+\infty$ $2512+00$ |  |
| $1265+01$ | 100 Et +04 | -7.28E+03 | 1.14E+03 | 8 83E+02 |  | $382 \mathrm{t}+02$ | 4 62E-04 | - 80E-04 | 793 | $2.93 \mathrm{E}-04$ | 1.30E-04 | $370 \mathrm{E}-\mathrm{S}$ | 1.74E-08 | $1.12 \mathrm{E}-01$ | 251 E 2. $70 \in+03$ | $1.20 E+\infty$ |
| $100 \mathrm{~F}+01$ | $108 E+04$ | -53E+03 | 1 2EE+03 | $988 \mathrm{E}+02$ |  | $4.70 E+02$ | 4 06E-04 | 0 36E-0 | 6 30E-01 | 2.706 .04 | 1.21E-04 | $420 \mathrm{E}-08$ | 1.02 cos | 1.288 .01 |  |  |
| $796 E+00$ | 1.17E+04 | + 96E+03 | 1. $338+03$ | 1.13E+03 |  | $573 \mathrm{E}+02$ | 3.57E-04 | $704 \mathrm{E}-04$ | 6.00E+01 | $253 \mathrm{E}-\mathrm{O}$ | 1 03E-04 | 8 OSECO | 206E-0 | 1.148 | $3008+\infty$ 3006 | $1.36 E+\infty$ $7.306+\infty$ |
| $632 E+\infty$ $502 E+\infty$ | 1.28E+04 | -1.18E+0 | 1.45E+63 | 1.31E $+\infty 3$ |  | 6 96E +02 | $3.15 \mathrm{E}-04$ | 8 85E-04 | 397 E | 2 40E-04 | 4.75E-C | cose-08 | 2.206-00 | 1.506-09 | 360E+C3 | 1. 3 SE+09 |
| $\begin{aligned} & 502 E+\infty 0 \\ & 300 E+\infty 0 \end{aligned}$ | 135E+04 | $-1.20 \mathrm{E}+0$ $-1.57 \mathrm{E}+0$ | $1.53 E+03$ | 1.46E+03 |  | $7.78 \mathrm{E}+02$ | 2.4E-04 | 5.33E-04 | 3.16E | $225 \mathrm{E}-04$ | 4 30E-C5 | 7.125-08 | 1.30E-96 | $17 \mathrm{EE}-01$ | $4206+\infty$ | -37E 92 |
| $3.17 \mathrm{E}+\infty$ | 1.74E+0A | -1.70eto4 | $197 \mathrm{E}+\infty$ | 203E+03 |  | $\begin{aligned} & 1.04 E+03 \\ & 1 \\ & 22 E+03 \end{aligned}$ | 2.45E-04 $2.8 E-04$ | ${ }^{4} 10 \mathrm{E}$ |  | $2.25 \mathrm{E}-04$ | 7.34E-05 | 397E-06 | 298E-06 | $2.00 \mathrm{E}-98$ | -02E 403 | 1.31E+03 |
| $2525+00$ | 1.05E+04 | $2.05 E+04$ | $2.21 E+\infty$ | 233 tc |  | 1. $185+\infty$ | $193 \mathrm{E}-04$ | 300 E - 4 | 158 E |  |  | 1.10E-08 | 2.71E.08 | 2246 -01 | $432 \mathrm{E}+03$ | $107 \mathrm{E}+03$ |
| $2.00 \mathrm{E}+00$ | OE+O | -2.35E+0 | $2.48 \mathrm{E}+03$ | $2.87 \mathrm{E}+03$ |  | 1.74E+03 | 171E-04 | $203 \mathrm{E}-04$ | 1.2 | $210 E-04$ | 4 37E-05 | 1.35E-05 |  | $2.518-09$ | 4.48E +03 | $1008+03$ |
| $1506+00$ | 2.47E+04 | $2.68 \mathrm{E}+04$ | $2.00 E+03$ | $304 E+03$ |  | $204 \mathrm{E}+03$ | 1.52E-04 | 2 27E-04 | - $98 \mathrm{E}+\infty$ | 206E-04 | 3 84E-05 | 208E-0 | 305E-0 |  | 4.87E | 0. $385+03$ |
| 1286500 | $270 E+04$ | $306 E+04$ | $316 \mathrm{E}+03$ | $347 \mathrm{E}+03$ |  | $240 \mathrm{E}+03$ | 1.35E-04 | $195 E-04$ | 7 93E $+\infty$ | $203 \mathrm{E}-04$ | 3 S8E-05 | 2 56E-D | ${ }^{\text {S }}$ SE-CO | 3 36E-01 | - $7 \times E+\infty$ | $7 S E+\infty$ 4 C+CO |
| $100 \mathrm{E}+0$ | Eto | 3 48E+C | $361 E+03$ | $395 E+03$ |  | $286 E+03$ | $120 \mathrm{E}-04$ |  | 6 30E+ ${ }^{\text {cos }}$ | 200 E -0r | 3 48E-05 | 317 E -0 | 5 SUE-08 |  |  | $4 E+\infty$ $47 E+\infty$ |
| 7 96E-01 | 3 S5E+04 | ง.91E404 | $402 \mathrm{E}+03$ | $447 \mathrm{E}+03$ |  | $3.27 \mathrm{E}+03$ | $107 \mathrm{E}-04$ | 1 48E-04 | 5 OOE $+\infty$ | 1.94E-O4 | 3 25E-0 |  | C $500 \times 0$ | S 47 E -01 | - |  |
| $632 \mathrm{E}-01$ | $404 E+04$ | $144 \mathrm{E}+04$ | $458 \mathrm{E}+03$ |  |  | $382 \mathrm{~F}+03$ | 9 57E-05 | $128 E-04$ | $397 \mathrm{E}+\infty$ | $180 \mathrm{E}-\mathrm{O}$ | $308 \mathrm{E}-5$ | 4 7eE-C | THE-0] | C $47 E-01$ | OOE $+\infty 3$ $13 E+\infty$ | 3SE 002 $32 E+02$ |
| 502 E .01 | 4 63E+04 | $500 E+04$ | 5 25E+03 | $578 E+03$ |  | $450 E+03$ | 8 83E-05 | 108 E -04 | $316 \mathrm{E}+\infty$ | 1 8BE-04 | 3.45E-08 | 8 07E-05 |  |  |  |  |
| 3 Pee-01 | 5.21E+04 | 5 cretor | $590 \mathrm{e}+03$ | - 30E+03 |  | $515 E+03$ | 7.65E.05 | 9 48E-05 | $2.51 \mathrm{E}+\infty$ | 1.83E-O4 | 3 35E-85 | 7.29E-05 | 10E-05 | $863 \mathrm{E}-01$ 132 Caj | $514 E+\infty$ 8.32E |  |
| $3.17 \mathrm{E}-09$ | $591 \mathrm{Et04}$ | ${ }^{6} 45 E+04$ | $671 E+03$ | 7.32E+03 |  | $585 E+03$ | 869E-05 | 8 2se-05 | 1.00E $+\infty$ | i.me-or | 3.53E-08 |  | 1.75E-06 | 7 Oee-0 |  |  |
| 2 52E-01 $200 \mathrm{E}-01$ | $717 E+04$ | $-770 E+04$ -7 | 8 13E+03 | 6. $74 \mathrm{E}+03$ 000503 |  | $737 \mathrm{E}+03$ | S 64E-05 | S ESEES | 1.58E $+\infty$ | 1.75E-04 | 3 95E-05 | 1.11E-04 | 250505 | $7.06 \mathrm{E}-01$ | 1 CNE.03 | $122 E+\infty$ |
| $1506-01$ | - SBE.04 | -10E+O4 |  | 1.00E |  | $7.71{ }^{\text {c/03 }}$ | 5 4 4 E-0 | S41E-05 | 1.26E $+\infty$ | 1 104E-04 | 3 50E.05 | 1.30E-04 | 2 83E-05 | C.92E-01 | $583 E+\infty 3$ | 1.28E 103 |
| 1 28E-01 | 973 | -1 O4E+05 | 1.10E*O4 | 1.18E+04 |  | 103 | $420 \mathrm{E}-55$ | 48 |  | 1 Set-o | 3.7EE- | 1set-04 | 3,70e-05 | $1.00 E+\infty$ | $895 E+03$ | $1415+\infty$ |
|  |  |  | +04 | 1.3E+04 |  | $1.17 \mathrm{E}+04$ | 3 00E-05 | 4.23E-05 | . 28 |  |  |  | 4 OE-08 | 112 tan | ${ }^{\text {coec }}$ | 1 SUE+03 |
|  |  |  |  |  |  |  |  |  |  |  | 38 |  |  | $128 E+\infty$ | SOE+ | 1.07E |







 $200 E+02762 E+03+44 E+02: 64 E+02 \quad 57 E+01$ $\begin{array}{llll}1.205 E+02 & 7.70 E+03 & -9.94 \mathrm{E}+02 & 174 \mathrm{E}+02 \\ 1.13 \mathrm{E} & 1.13 \mathrm{E}+02\end{array}$ $\begin{array}{llll}1.00 E+02 & 783 E+03 & -1.37 E+03 \\ 1.000 E+02 & 1.55 E+02\end{array}$ 7.06E+01 COOE +033 -1 COE +03 O 14E+02


 2.52E $2019.25 E+\infty 3$




 $\begin{array}{ccccc}5.02 E+00 & 1.40 E+04 & \text { f } 50 E+03 & 168 E+03 & 74 E+00 \\ 390 E & 162 E+04 & +37 E+\infty & 183 E+03 & 106 E+00\end{array}$
 $\begin{array}{lllll}2.52 E+\infty & 1.85 E+04 & -1.00 E+04 & 221 E+01 & 122 E+03\end{array}$ $\begin{array}{llll}2.00 E+\infty & 2.12 E+04 & -1.13 E+\infty 4 & 2.41 E+03 \\ 1.50 E+\infty & 1.28 E+03 \\ 231 E+04 & -1.18 E+04 & 262 E+03 & 1.33 E+\infty 3\end{array}$
 1.00E +00 2.00E $+04-1.24 E+04$ S.06E +03 1.41E+00 $796 E-01200 E+04-1.28 E+043.28 E+03 \quad 1.46 E+03$ O.32E-O1 $300 E+94-1.30 E+04351 E+09140 E+00$
 3.17E.01 3.05E+04-1 $41 E+044.14 E+0391.50 E+00$
 2.00E-01 $406 E+04$-1 52E+04 4 C0E +03 $\quad 1.72 E+03$ $150 E-01427 E+04$-1 $60 E+04484 E+03 \quad 1.01 E+03$


$\begin{array}{cccc}145 E+\infty & 208 E-02 & 747 E-02 \\ 755 E+00 & 126 E-02 & 389 E-02\end{array}$ $127 E+01108 E-02$ 2.72E-02 $\begin{array}{llll}181 E+01 & 8.31 E-03 & 1.97 E-02 \\ 230 E+01 & 172 E-03 & 153 E\end{array}$ $\begin{array}{cccc}230 E+01 & 672 E-03 & 153 E-02 \\ \text { 3.08E+01 } & 5.06 E-00 & 1.23 E-02\end{array}$ $385 \mathrm{E}+0144.62 \mathrm{E}-03 \mathrm{~S}$ 1.01E-02 4 74E+01 4 15E-03 : 3OE-03 B.70E+011 1.57E-03 7.07E-0 . $88 \mathrm{E}=01$ 3.08E-0 $5.05 E-03$ 21E4 $2.67 \mathrm{E}-008$ S.04E-0 | $77 E+01$ | $2.30 E-\infty 0$ | $427 E-03$ |
| :---: | :---: | :---: |
| $16 E+02$ | 1 | $18 E-03$ |
| $.03 E-03$ |  |  | $\begin{array}{lll}1.16 E 00 & 188 E-01 & 3.03 E-03 \\ 1.32 E+\infty & 1.41 E-03 & 1.12 E-03\end{array}$ 1.03E+02 $1.40 E-\infty 8$

 $\begin{array}{llll}235 E+02 & 1.11 E-03 & 1.00 E-03\end{array}$
 4.00E+002 7 7SEE-04 $1.14 E-03$


 $\begin{array}{lll}1.00 E+02 & 800 E-04 & 577 E-04 \\ 1.02 E+03 & 4.70 E-04 & 4.91 E-04\end{array}$ 120E+03 A SEE-O4 4.17E-04 $1.30 E+003408 E-04$ S $57 E-04$ $150 \mathrm{E}+0 \mathrm{O} 381 \mathrm{E}-\mathrm{OH}$ 3.07E-O4 $1.006+033$ S.58E-04 $285 E-04$
 $248 E+03$ S $301 E-04$ 1.7BE-O4 $20 E+\infty 3285 E-041.57 E-04$ $285 E+0382.73 E-041.42 E-04$ $\begin{array}{lll}1.12 E+03 & 250 E-04 & 1.20 E-04 \\ 33 E+03 & 244 E O 4 & 19 E-04\end{array}$ $\begin{array}{lll}333 E+03 & 24 E E-04 & 1.18 E-04 \\ 3.57 E+03 & 232 E-A 4 & 100 E-04\end{array}$ 3. TOE $+\infty$ 2. 20 EE -04 OTE-D
 $\begin{array}{lll}425 E+00 & 108 E-04 & 8.74 E-05 \\ 4.52 E+03 & 1.05 E-04 & 1.10 E-05\end{array}$





\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|c|}
\hline frequency \& Z \& Z" \& 2\% \(1 \mathrm{~cm}^{2}\) \& 2"/cm \({ }^{2}\) \& \({ }^{\text {c }}\) \& 2'Rs \& \(r\) \& \({ }^{\prime \prime}\) \&  \& \(r\) \& \(r^{\prime \prime}\) \& r/e \& rmo \& 1/sqri(w) \& ( \()^{1}\) \& 1/0c(s) \\
\hline \(200 E+03\) \&  \& \(217 \mathrm{E}+02\) \& 7 52E+02 \& -2 46E+01 \& 7.55E+02 \& \(295 \mathrm{E}+00\) \& SOE-03 \& \[
-401 E-02
\] \& \[
126 E+04
\] \& S 97E-03 \& \[
318 E-03
\] \& S 16E-07 \& -2 53E-07 \&  \&  \& \[
-1.23 E+02
\] \\
\hline \(150 \mathrm{E}+03\) \& 6 64E+03 \& - \(82 \mathrm{E}+01\) \& \(754 \mathrm{E}+02\) \& -1 11E+01 \& \& \(-127 \mathrm{E}+00\) \& \[
-101 E-02
\] \& \[
+86 E .02
\] \& \[
\begin{aligned}
\& \text { OREE+00 } \\
\& 0
\end{aligned}
\] \& \[
-257 E-02
\] \& \[
-147 \mathrm{E}-02
\] \& \begin{tabular}{l}
\(\rightarrow 18 E-07\) \\
-2 58E-08
\end{tabular} \& - 2 53E-07 \& \[
\begin{aligned}
\& 0 \quad 02 E-03 \\
\& 1.00 E-02
\end{aligned}
\] \& -1 54E+02 \& -1.23E+02 \\
\hline \(1.28 \mathrm{E}+03\) \& 6 coeto3 \& -1.37E+01 \& 7 55E+02 \& 1.55E+00 \& \& \(105 \mathrm{E}-01\) \& 7.00E-02 \& \(636 \mathrm{E}-01\) \& \(793 \mathrm{E}+03\) \& -3 94E-02 \& - \(106 E-01\) \& - 2 S8E-06 \& - \(448 \mathrm{E}-00\) \& \(1.00 \mathrm{E}-02\)
\(112 \mathrm{E}-02\) \& -1.38E+01 \& \\
\hline \(100 \mathrm{E}+03\) \& 8 88E+03 \& \(-1.20 E+02\) \& 7 57E +02 \& 1.36E+01 \& \& \(220 \mathrm{E}+00\) \& 1 16E-02 \& 7.17E-02 \& \(630 \mathrm{E}+03\) \& \(304 \mathrm{E}-03\) \& -1 94E-02 \& \({ }^{4} 82 \mathrm{EE-07}\) \& - \({ }^{\text {S }}\) OTE-00 \& 1.2E-02 \& \(1780 E-01\)
\(780 E+00\) \& -2.13E+00 \\
\hline \(796 \mathrm{E}+02\) \& 6 70E+03 \& -2 16E+02 \& 7 59E+02 \& 2 45E+01 \& \& \(448 \mathrm{E}+00\) \& 7 25E-03 \& \(396 \mathrm{E}-02\) \& \(500 \mathrm{E}+03\) \& \(270 \mathrm{E}-03\) \& \(\rightarrow 91 \mathrm{E}-03\) \& 8 40E-07 \& -178E-00 \&  \& \[
312 E+01
\] \& -1 O3E+02 \\
\hline \(632 \mathrm{E}+02\) \& \(672 \mathrm{E}+03\) \& -2.00E+02 \& 7 62E +02 \& 3 29E+01 \& \& \(7.28 \mathrm{E}+00\) \& \({ }^{6} 40 \mathrm{E}-03\) \& 2 20E-02 \& \(397 E+03\) \& \(248 \mathrm{E}-03\) \& -5 E6E-03 \& 8 24E-07 \& -174E-0 \& \(141 E-02\)
\(150 E-02\) \& \(312 E+01\)
S \(14 E+01\) \& \(-103 E+02\)
\(-145 E+02\) \\
\hline \(502 \mathrm{E}+02\) \& \(675 E+03\) \& 410 E 02 \& 7 88E+02 \& 4 65E+01 \& \& \(110 \mathrm{E}+01\) \& 4 60E-03 \& \(204 E-02\) \& \(316 \mathrm{E}+03\) \& 2 14E-03 \& -3 30E-03 \& \& \& \& \& \\
\hline 3 99E+02 \& 8 80E+03 \& -5 71E+02 \& \(771 \mathrm{E}+02\) \& 6 48E+01 \& \& \(1.61 \mathrm{E}+01\) \& 3 62E-03 \& 1 45E-02 \& \(251 \mathrm{E}+03\) \& 2 20sE-03 \& -1 23E-03 \& - 268 E-07 \& - \({ }^{-104 E-08}\) \& \(178 E-02\)
\(200 E-02\) \& \(138 E+02\)
\(37 E+02\) \& -2 14E+02 \\
\hline \(317 \mathrm{E}+02\) \& 6 8SE+03 \& \(-722 \mathrm{E}+02\) \& \(77 \mathrm{E}+02\) \& 19E+01 \& \& \(219 \mathrm{E}+01\) \& 3 05E-03 \& 1.14E-02 \& \(199 E+03\) \& 1.77E-03 \& -S B0E-04 \& 8 86E-07 \& - \(314 \mathrm{E}-07\) \& \(200 E-02\)
\(224 \mathrm{E}-02\) \& 3.92E+02 \& -2 11E+02 \\
\hline \(252 \mathrm{E}+02\) \& \(601 \mathrm{E}+03\) \& \(\rightarrow\) 95E+02 \& \(784 \mathrm{E}+02\) \& 101E+02 \& \& \(289 E+01\) \& \(2605-03\) \& -12E-03 \& 1.58E+03 \& 1.56E-03 \& - 3 24E-04 \& 885E-07 \& -2 05 E -07 \& \(224 E-02\)
\(251 E-02\) \& \(4.02 \mathrm{E}+02\)
6.15E+02 \& -1 \(189 E+02\) \\
\hline \(200 \mathrm{+}+02\) \& 6 98E+03 \& -1.10E+03 \& \(792 \mathrm{E}+02\) \& 1.24E+02 \& \& \(375 E+01\) \& \(223 E-03\) \& 7.38E-03 \& 1.28E+03 \& 1.97E-03 \& -5.73E-05 \& 1 09E-08 \& \(-205 E-07\)
\(-150 E-08\) \& 2 S1E-02
\(282 \mathrm{E}-02\) \& \({ }^{6} 1.15 \mathrm{C}+02\) \& -1 \(308 \mathrm{E}+01\) \\
\hline 1 59E+02 \& \(7.08 \mathrm{E}+03\) \& -1 32E+03 \& \(803 \mathrm{E}+02\) \& \(150 \mathrm{E}+02\) \& \& 479 EPOY \& \(193 \mathrm{E}-03\) \& C OSE-03 \& 9 98E+02 \& \(1.18 \mathrm{E}-03\) \& 1.08E-04 \& \(118 \mathrm{E}-08\) \& 108E-07 \& \(281 \mathrm{E}-02\)
\(3.17 \mathrm{E}-02\) \& ( \(30 \mathrm{E}+02\) \& 7.61E+01 \\
\hline \(1.28 \mathrm{E}+02\) \& \(7.19 \mathrm{E}+03\) \& -1 59E+03 \& 4.15E+02 \& \(180 \mathrm{E}+02\) \& \& 6 OUE+01 \& 1 67E-03 \& \(498 \mathrm{E}-03\) \& 7 93E+02 \& \(101 \mathrm{E}-03\) \& \(2086-04\) \& 1.28E-08 \& \(262 \mathrm{E}-07\) \& 3 SSE-02 \& \({ }^{1}\) 48E+02 \& 1.95E+02 \\
\hline 1 100E+02 \& 7.33E+03 \& -1 \(81 \mathrm{E}+03\) \& a 311 +02 \& \(218 E+02\) \& \& 7 59E+01 \& \(14 \mathrm{EE-03}\) \& 4 12E-03 \& \(630 E+02\) \& © 82E-04 \& \(201 E-04\) \& 1.40E-06 \& \(262 E-07\)
\(402 E-07\) \& 3 96EE-02 \& \(1{ }^{\text {a }}\) \&  \\
\hline 7 96E+01 \& \(749 \mathrm{E}+03\) \& \(-2.28 \mathrm{E}+03\) \& \(849 E+02\) \& 2 58E+02 \& \& \(946 E+01\) \& 1 25E-03 \& \(341 \mathrm{E}-03\) \& \(500 E+02\) \& 7 85E-04 \& 3.23E-04 \& 1.53E-08 \& \(4.62 E-07\)
8 4SE-07 \&  \&  \&  \\
\hline \(632 \mathrm{E}+01\) \& 7 89E+03 \& \(-271 \mathrm{E}+03\) \& : 72E+02 \& \({ }^{3} 07 \mathrm{E}+02\) \& \& 1.17E+02 \& 1.08E-03 \& 2 85E-03 \& 3 97E+02 \& 6 coe-04 \& \(3 \mathrm{SOE-O}\) \&  \& \% 40E-07 \& 5 S02E-02 \& \(111 \mathrm{E}+03\) \& 4 caetoz
11EP02 \\
\hline \(502 \mathrm{E}+01\) \& 7 182E+03 \& -3.27E+03 \& 198E+02 \& 3.71E+02 \& \& \(143 \mathrm{E}+02\) \& - 05E-04 \& 2 35E-03 \& 3 18E+02 \& 8.53E-04 \& \(308 \mathrm{E}-04\) \& 1.75E--8 \& 989E-07 \& 5 S \(63 E-02\) \&  \& 7.6EE \({ }^{\text {coz }}\) \\
\hline 3 99E+01 \& 8 23E+03 \& \(-318+03\) \& \(934 \mathrm{E}+02\) \& \(432 \mathrm{E}+02\) \& \& \(1.79 E+02\) \& : 10E-04 \& 1.90E-03 \& \(251 \mathrm{E}+02\) \& 4.78E-04 \& 9.23E-04 \& (175E-06 \& \(969 \mathrm{E}-07\)
\(1.20 \mathrm{E}-08\) \& 5 83E-02
\(632 \mathrm{~S}-02\) \&  \& \(7.66 E+02\)
\(.67 E+02\) \\
\hline \(317 \mathrm{E}+01\) \& \(861 E+03\) \& \(\rightarrow\) S1E+03 \& 9 77E+02 \& 511 E 02 \& \& \(2.22 \mathrm{E}+02\) \& \(714 \mathrm{E}-04\) \& \(1.65 E-03\) \& 1 99E+02 \& \(409 \mathrm{E}-04\) \& \(3.23 \mathrm{E}-04\) \& 2 OSE-00 \& \(1.20 E-06\)
\(1.52 \mathrm{E}-06\) \& \({ }_{7} 7\) 32EE-02 \& \(1.44 E+03\)
\(158 E+03\) \& ¢ \(67 \mathrm{E}+02\)
1.17E +03 \\
\hline \(252 \mathrm{E}+01\) \& \(108 \mathrm{E}+03\) \& . 5 30E+03 \& \(1.03 E+03\) \& \(601 \mathrm{E}+02\) \& \& \(273 \mathrm{E}+02\) \& 6 25E-04 \& 1.38E-03 \& 1.58E+02 \& 3 50E-04 \& \(273 \mathrm{E}-04\) \& \(222 \mathrm{E}-08\) \& \(172 \mathrm{E}-08\) \& \& \& \\
\hline \(2.00 \mathrm{E}+01\) \& \(861 E+03\) \& - 23E+03 \& \(1.09 E+03\) \& \(707 \mathrm{E}+02\) \& \& \(335 \mathrm{E}+02\) \& 5.48E-04 \& 1.15E-03 \& 1.26E+02 \& 3 03E-04 \& \(243 \mathrm{E}-04\) \& \(205 \mathrm{E}-06\)
241 Cos \& \(172 E-06\)
\(103 E-08\) \& \(709 E-02\)

$6.92 E-02$ \& $1.78 E+03$
$201 E+03$ \& $1.38 E+03$
$101 E+03$ <br>
\hline $1.59 \mathrm{E}+01$ \& $101 \mathrm{E}+04$ \& -7.08E+03 \& 1.15E+03 \& $803 \mathrm{E}+02$ \& \& $395 \mathrm{E}+02$ \& $493 \mathrm{E}-04$ \& $100 \mathrm{E}-03$ \& - 90E+01 \& 2 56E-04 \& 1.79E-04 \& 2.57E-06 \& 1.79E-06 \& 8.92E-02 \& $201 \mathrm{~L}+03$ \& 1.81E+03 <br>

\hline $1.26 \mathrm{E}+04$ \& 111 E 04 \& -6 49E+03 \& $1.25 E+03$ \& 9 82E+02 \& \& $499 \mathrm{E}+02$ \& 4 25E-04 \& 1 19E-04 \& 7 93E+01 \& 2 41E-04 \& $178 \mathrm{E}-04$ \& $304 \mathrm{E}-08$ \& $225 \mathrm{E}-08$ \& $1.12 \mathrm{E}-01$ \& $$
280 E+03
$$ \& 1. $23 E+03$ <br>

\hline $100 \mathrm{E}+01$ \& $120 \mathrm{E}+04$ \& - $85 \mathrm{E}+03$ \& 1.36E+03 \& $112 \mathrm{E}+03$ \& \& $607 \mathrm{E}+02$ \& 3.75E-04 \& 6 O1E-04 \& 6 30E+01 \& 2 21E-04 \& 1 150.-04 \& 3.51E-06 \& $225 E-06$
$238 E-08$ \& 1.12E-01 \& $280 \mathrm{E}+03$
$310 \mathrm{ta3}$ \& 1.98E 03
2. $10 \mathrm{E}+03$ <br>
\hline $708 \mathrm{E}+00$ \& 1.31E+04 \& -1.14E+04 \& $148 E+03$ \& 1.29E+03 \& \& 7 30E+02 \& 3 32E-04 \& 5 87E-04 \& 5 O0E+01 \& $2.08 \mathrm{E}-04$ \& 1.24E-04 \& 412E-06 \& \& \& \& 2.10E+03
$214 \mathrm{E}+03$ <br>
\hline 6.32E+00 \& $14 \mathrm{AE}+04$ \& -1 31E+04 \& $1.83 E+03$ \& 1.49E+03 \& \& \% $77 \mathrm{E}+02$ \& $294 \mathrm{E}-04$ \& 4 99E-04 \& 3 97E+01 \& 1 95E-04 \& 1.04E-04 \& 4.22E-06 \& $248 \mathrm{E}-06$

261 E \& $1.41 \mathrm{E}-01$ \& 3.57E403 \& $$
\begin{aligned}
& 2 \text { LAE } 03 \\
& 2 ~ 12 E \cdot 03
\end{aligned}
$$ <br>

\hline $502 \mathrm{E}+00$ \& $1.50 \mathrm{E}+04$ \& -1 51E+04 \& $1.81 \mathrm{E}+03$ \& 1.71E+03 \& \& $1.05 \mathrm{E}+03$ \& 2 20E-04 \& $424 \mathrm{E}-04$ \& 318 E 01 \& $188 \mathrm{E}-04$ \& B77E-05 \& $594 \mathrm{E}-00$ \& $278 E .00$ \& 1.70E-01 \& 4.30E+03 \& $212 E+03$
$204 E+03$ <br>
\hline 3 98E+00 \& $1.79 \mathrm{E}+04$ \& -1.75E+04 \& $203 E+03$ \& 199E+03 \& \& $1.28 \mathrm{E}+03$ \& $229 \mathrm{E}-04$ \& 3.57E-04 \& 251 E+01 \& 1.84E-04 \& 7 98E-05 \& 7.32E-08 \& S $317 \mathrm{E}-\infty$ \& $200 \mathrm{E}-01$ \& 4.30E+03 \& $204 E+03$
$109 E+03$ <br>
\hline $317 \mathrm{E}+00$ \& 1,09E+04 \& -1 99E+04 \& 2 25E+03 \& $2286+03$ \& \& $1.50 \mathrm{E}+03$ \& 2 OUE-04 \& 3 07E-04 \& 1.00E+01 \& 1.78E-04 \& C61E-03 \& 1.93E-06 \& \& \& \& $100 \mathrm{E}+03$ <br>

\hline $252 \mathrm{E}+00$ \& $222 \mathrm{E}+04$ \& $227 \mathrm{E}+04$ \& 2 52E+03 \& $258 \mathrm{E}+03$ \& \& $1.77 \mathrm{E}+03$ \& 1.01E-04 \& $264 \mathrm{E}-04$ \& 1.58E+01 \& 1.74E-04 \& 5.68E-05 \& -.93E-06 \& | $3.32 \mathrm{E}-06$ |
| :--- |
| 358 C | \& $224 \mathrm{E}-01$ \& 4 9ME+03

$8.20 E+03$ \& $184 E+03$
$1,60 E+03$ <br>
\hline $200 E+\infty$ \& 2 S0E+04 \& -2 59E+04 \& $283 E+03$ \& $293 \mathrm{E}+03$ \& \& $208 \mathrm{E}+03$ \& 1.61E-04 \& $2.27 \mathrm{E}-04$ \& 1.28E+01 \& 1.70E-04 \& 4 93E-05 \& 1.35E-0s \& 3.92E-08 \& $2.51 \mathrm{E}-01$ \& 8.20E403 \& 1,60E 0 O3 <br>
\hline $159 \mathrm{E}+\infty$ \& 2 B0E+04 \& -2 $93 \mathrm{E}+04$ \& 3.18E+03 \& 3 33E+03 \& \& $242 \mathrm{E}+03$ \& $1.43 \mathrm{E}-04$ \& $196 \mathrm{E}-04$ \& -98E+00 \& $180 E-04$ \& 4.48E-05 \& 1 66E-05 \& 4.47E-06 \& $262 E-01$
$317 E-01$ \& 843 taO
862 C 03 \& $150 E+03$
$1.51 E+03$ <br>
\hline $1.26 \mathrm{E}+00$ \& $3.16 \mathrm{E}+04$ \& 3 32E+04 \& 3 58E+03 \& 3.77E+03 \& \& $2.83 \mathrm{E}+03$ \& $1.27 \mathrm{E}-04$ \& 1.70E-04 \& $7.93 \mathrm{E}+00$ \& 1 83E-04 \& $420 \mathrm{E}-05$ \& $200 \mathrm{E}-05$ \& 8.30E-06 \& 3 s5E-01 \& 862E+03 \& 1.81E+03 <br>
\hline $100 \mathrm{E}+00$ \& 3 SEE+04 \& 3 75E+04 \& 4 06E+03 \& $425 \mathrm{E}+03$ \& \& 3.31E+03 \& 1.14E-04 \& $147 \mathrm{E}-08$ \& $630 \mathrm{t}+0$ \& 1.50E-04 \& $378 \mathrm{E}-0 \mathrm{~S}$ \& 2 53E-05 \& S.30e-06
$8.8 \mathrm{E}-08$ \& 3 5SE-01 \& S.75E+03 \& 1.48Et03 <br>
\hline $7.96 \mathrm{E}-01$ \& $401 E+04$ \& -4.24E+04 \& 4 55E+03 \& 4 81E+03 \& \& 9.79E+03 \& t.01E-04 \& 1.28E-04 \& 8 00E+00 \& 1.50E-04 \& $371 \mathrm{E}-05$ \& 3.11E-05 \& 7.42E-06 \& 4.47E-01 \& $884 \mathrm{Et03}$
0 OEf03 \& $1.40 E+03$
$1.45 E+03$ <br>
\hline 0 32E-09 \& $4.51 \mathrm{E}+04$ \& $479 \mathrm{E}+04$ \& $311 E+03$ \& 5.43E+03 \& \& 4.35E+03 \& $899 \mathrm{E}-05$ \& 1.12E-04 \& 3 97E +00 \& 1.52E-04 \& 3 S4E-03 \& \& \& \& \& 1.45E+03 <br>
\hline 5 02E-09 \& $514 \mathrm{E}+04$ \& -64E+04 \& 5 B3E+03 \& $817 E+03$ \& \& $507 \mathrm{E}+03$ \& $795 \mathrm{E}-05$ \& - 87 E -05 \& $318 E+\infty 0$ \& 1.40E-04 \& 3 3 4EE-05 \& 3 33E-03 \& $8.80 \mathrm{E}-06$
$1.08 \mathrm{E}-05$ \& $802 E .01$
$883 E .01$ \& $824 E+03$
$40 E+03$ \& 1.45E+03 <br>
\hline 3 P9E-01 \& $578 \mathrm{E}+04$ \& - 03E+04 \& 6.55E+03 \& 684E+03 \& \& $580 E+03$ \& 7.22E-05 \& 9 51E-05 \& $2.51 \mathrm{E}+0$ \& 1.43E-04 \& 3 308E-05 \& 8 $71 \mathrm{E}-05$ \& 1.06EE-05

1 46E-05 \& | 863 E .01 |
| :--- |
| 632 E | \& ${ }_{8}$ \& 147 ECOS

168 COS <br>
\hline 3 17E-01 \& 6 43E+04 \& - $05 \mathrm{E}+04$ \& $730 \mathrm{E}+03$ \& 7.69E+03 \& \& $654 \mathrm{E}+03$ \& 6.23E-05 \& 7.51E-05 \& \& 1.39E-04 \& 3 S2E-05 \& 8 07E-05 \& $177 \mathrm{E}-05$ \& $7.09 \mathrm{E}-01$ \& C $77 E+09$ \& $1{ }^{1}$ <br>
\hline 2 52E-01 \& $722 \mathrm{E}+04$ \& $.776 \mathrm{E}+04$ \& $518 \mathrm{E}+03$ \& 800E+03 \& \& $7.43 E+03$ \& $580 \mathrm{E}-05$ \& 8 C4E-05 \& $158 E+\infty$ \& 1 1 35E-04 \& 3 S2E-OS
3 S0E-05 \& 8 52 E E-05 \& $177 \mathrm{E}-05$
$221 E-08$ \& $7.09 E-01$

$705 \mathrm{E}-01$ \& $$
\begin{aligned}
& \text { 6.77E+03 } \\
& 605 E+03
\end{aligned}
$$ \& $1.72 \mathrm{EcO3}$

$1006+03$ <br>
\hline $200 \mathrm{E}-01$ \& $824 \mathrm{E}+64$ \& + 44E+04 \& 9.34E+03 \& 9.57E+03 \& \& 8.58E+03 \& 5.19E-05 \& 3.79E-05 \& 1.28E +00 \& 1.28E-04 \& 3 53E-95 \& 1.02E-94 \& 2 21E-0S \& 8.02E-01 \& \& 1206003
$201 E+03$ <br>

\hline $1.59 \mathrm{E}-01$ \& - 37E+04 \& - 0 ese+04 \& $108 \mathrm{E}+04$ \& $112 \mathrm{E}+04$ \& \& $987 \mathrm{E}+03$ \& 4 4E-05 \& S.03E-05 \& 0 98E-01 \& $123 \mathrm{E}-04$ \& $352 \mathrm{E}-05$ \& 1.23E-04 \& 3.53E-05 \& $$
100 \in+\infty
$$ \& \& $201 E 603$

$2.15 E+03$ <br>
\hline $126 \mathrm{E}-01$ \& 1.03E+05 \& -1.12E+05 \& 1.90E+04 \& 1.27E+04 \& \& $1.11 \mathrm{E}+04$ \& 3.89E-05 \& 4.45E-05 \& 7.03E-01 \& 1.17E-04 \& ${ }^{3} \mathbf{6 2 E - 0 5}$ \& 1.47E-04 \& 4.57E-0s \&  \& 7 $716+03$ \& 2.15E+03 <br>
\hline 1 00E-01 \& 1.18E+05 \& -1 26E+0S \& 1.34E+04 \& 1.43E+04 \& \& $1.27 \mathrm{E}+04$ \& 3.47E-05 \& 3 92E-05 \& 6.28E \& 1.10 -6 \& 3644 \& 1.758 \&  \& .122E+00 \&  \& $242 \mathrm{E} \cdot 03$ <br>
\hline With ET roagork \& \& \& \& \& \& \& \& \& \& \& $304 \mathrm{E}-\mathrm{S}$ \& 1.75E-4 \& \& 1.20E \& \& $272 \mathrm{E}+03$ <br>
\hline $200 \mathrm{E}+03$ \& 719 E 03 \& 1.08E+02 \& 2.15E+02 \& 2.22E401 \& 6.20E+02 \& $451 \mathrm{E}+00$ \& 4.77E-03 \& - 32E.02 \& \& \& \& \& \& \& \& <br>
\hline 1.59E+03 \& 7.21E+03 \& $659 E+01$ \& 8.17E+02 \& -7.48E+00 \& \& -2.17E+00 \& - $3.58 \mathrm{E}-02$ \& -1.23E-01 \& \& \& \& \& \& \& \& <br>
\hline $1.26 \mathrm{E}+03$ \& 7.24E+03 \& - 93E+01 \& B.21E+02 \& 3.59E+00 \& \& 1. $33 \mathrm{E}+\infty 0$ \& A DSE-02 \& 1 SoE-01 \& \& \& \& \& \& \& \& <br>
\hline $100 \mathrm{E}+03$ \& 7 27E+03 \& -1.56E+02 \& :24E+02 \& 1.77E+01 \& \& $4.98 \mathrm{E}+\infty 0$ \& $146 \mathrm{E}-02$ \& 5 23E-02 \& \& \& \& \& \& \& \& <br>
\hline $706 \mathrm{E}+02$ \& 731 E 03 \& 2 60E+02 \& 8 29E+02 \& 2 95E+01 \& \& $9.58 \mathrm{E}+00$ \& 1.95E-03 \& 3 07E-02 \& \& \& \& \& \& \& \& <br>
\hline 6 32E+02 \& 7 35E+03 \& 3.32E+02 \& - 34E+02 \& 3.77E+01 \& \& 1.45E+01 \& $188 E-03$ \& 2 31E-02 \& \& \& \& \& \& \& \& <br>
\hline $502 \mathrm{E}+02$ \& 741 E 03 \& $144 \mathrm{E}+02$ \& : $40 \mathrm{E}+02$ \& 3.03E+09 \& \& $2.05 E+01$ \& 6.94E-03 \& 1.71E-02 \& \& \& \& \& \& \& \& <br>
\hline 3 90E+02 \& 7.47E+03 \& -5 60E+02 \& $147 \mathrm{E}+02$ \& - 35E+01 \& \& $271 E+01$ \& $869 E-03$ \& 1.33E-02 \& \& \& \& \& \& \& \& <br>
\hline $317 \mathrm{E}+02$ \& 7.53E+03 \& -64E+02 \& 8.54E+02 \& 7.78E+01 \& \& 3 49E+01 \& $4.82 \mathrm{E}-03$ \& 1.07E-02 \& \& \& \& \& \& \& \& <br>
\hline 2 52E+02 \& $761 \mathrm{E}+03$ \& +20E+02 \& : 63 E+02 \& 9.30E+01 \& \& $439 E+01$ \& $4.16 \mathrm{E}-03$ \& 79E-03 \& \& \& \& \& \& \& \& <br>
\hline $200 E+02$ \& $770 \mathrm{E}+03$ \& - 70E+02 \& 8 74E+02 \& 1.10E+02 \& \& 5 41E+0¢ \& 3 60E-03 \& 7.32E-03 \& \& $\cdots$ \& \& \& \& \& \& <br>
\hline $1.50 \mathrm{E}+02$ \& 7 B0E+03 \& -1.14E+03 \& B5E+02 \& $1.29 E+02$ \& \& ( SAE 01 \& 3 12E-03 \& © 16E-03 \& \& \& \& \& \& \& \& <br>
\hline $1.28 \mathrm{E}+02$ \& 7.02E+03 \& -1 34E+03 \& - $98 E+02$ \& 1.52E+02 \& \& 7 E5E+01 \& $288 E-03$ \& $819 \mathrm{E}-03$ \& \& \& \& \& \& \& \& <br>
\hline $1.00 \mathrm{E}+02$ \& 8 OSE+03 \& -1.57E+03 \& - 13E+02 \& 1.78E 02 \& \& $9.37 \mathrm{E}+01$ \& 2 33E-03 \& 441E-03 \& \& \& \& \& \& \& \& <br>
\hline 7 98E+01 \& 3.21E+03 \& -1 83E+03 \& - 31E+02 \& $207 \mathrm{E}+02$ \& \& 1. $12 \mathrm{~F}+02$ \& $2.02 \mathrm{E}-03$ \& 3.74E-03 \& \& \& \& \& \& \& \& <br>
\hline $632 \mathrm{E}+01$ \& 6.40E+03 \& 2.13E+03 \& 9.52E+02 \& $2.42 \mathrm{E}+02$ \& \& 1.33E+02 \& $4.74 \mathrm{E}-03$ \& 3 16E-03 \& \& \& \& \& \& \& \& <br>
\hline $502 \mathrm{E}+01$ \& $883 \mathrm{E}+03$ \& $235 \mathrm{E}+03$ \& . $70 ¢$ ¢02 \& $200 \mathrm{E}+02$ \& \& $1.59 \in+02$ \& 1.48E-03 \& $265 E-03$ \& \&  \& \& \& \& \& \& <br>
\hline $3.99 \mathrm{E}+01$ \& $187 \mathrm{E}+03$ \& -2.91E+03 \& 1.01E+03 \& 3.30E+02 \& \& $1.66 E+02$ \& 1.30E-03 \& 2.30E-03 \& \& \& \& \& \& \& \& <br>
\hline $317 \mathrm{~F}+01$ \& Q.18E+03 \& $\rightarrow$ 40E+03 \& $104 \mathrm{E}+03$ \& 3 85E+02 \& \& $222 \mathrm{E}+02$ \& 4.12E-03 \& 1.95E-03 \& \& \& \& \& \& \& \& <br>
\hline 2.52E+01 \& 0.58E+03 \& -3 DeE 03 \& 1.08E+03 \& $440 E+02$ \& \& $2.55 E+02$ \& - $76 E-04$ \& 1.65E-03 \& \& \& \& \& \& \& \& <br>
\hline $2.00 E+01$
$1.50 \mathrm{E}+01$ \& 1.00E+04 \& - $4.60 \mathrm{E}+03$ \& 1.14E+03 \& 5.22E+02 \& \& $3.18 E+02$ \& $8528-04$ \& 1.40E-03 \& \& \& \& \& \& \& \& <br>

\hline $$
\begin{aligned}
& \text { 1.59E+01 } \\
& \text { 4.28E+01 }
\end{aligned}
$$ \& 1.08E+04 \& -6.32E+03 \& 1.20E-03 \& COEEAO2 \& \& 3 3 83E+02 \& 7.49E-04 \& 8.18E-03 \& \& \& \& \& \& \& \& <br>

\hline 1.26E+01

$100 \mathrm{E}+01$ \& $$
\begin{aligned}
& 1.13 E+04 \\
& 1.22 E+04
\end{aligned}
$$ \& -6.12E+03 \& 1.28E+03 \& $694 \mathrm{E}+02$

7 91E+02 \& \& $$
\begin{aligned}
& 463 E+02 \\
& 881 E+02
\end{aligned}
$$ \& 6 68E-O4

8 gek-04 \& 997E-04 \& \& $\infty$ \& \& \& \& $$
\mathrm{m}
$$ \& \& <br>

\hline $7.96 \mathrm{E}+00$ \& $1.32 \mathrm{E}+04$ \& -7 ${ }^{\text {a }}$ E+03 \& 1.50E+03 \& $894 E+02$ \& \& 6.77E+02 \& $538 \mathrm{E}-04$ \& 7.11E-04 \& \& \& \& \& \& \& \& <br>
\hline © 32E+00 \& 1.44E+04 \& $t 82 \mathrm{E} 03$ \& 1 8SE403 \& 1.00E+03 \& \& . 12 E ¢ 02 \& 4.SOE-O4 \& - 03 E -04 \& \& \& \& \& \& \& \& <br>
\hline 5.02E +60 \& 1.58E+04 \& + $76 E+03$ \& 1.79E+03 \& 1.11E+03 \& \& - 68E+02 \& 4.48E-04 \& 8.12E-p4 \& \& \& \& \& \& \& \& <br>
\hline 3 99E +00 \& 1.73E+04 \& -1 07E+04 \& 1.96E+03 \& 1.21E+03 \& \& 1.14E+03 \& 4.12E-04 \& $436 E-04$ \& \& 0 \& \& \& \& \& \& <br>
\hline $3.17 \mathrm{E}+\infty$ \& 1.90E+04 \& -1.15E+04 \& 2 16E+03 \& $131 \mathrm{E}+03$ \& \& 1.34E+03 \& $382 \mathrm{E}-4$ \& 3.74E-04 \& \& \& coen 4 \& cos. \& 10 \& 101 \& \& <br>

\hline $2.52 \mathrm{E}+00$ \& 2.09E+04 \& -1.24E+04 \& 2.37E+03 \& 1.40E+03 \& \& 1.55E+03 \& 3 SEE-04 \& 3.21E-04 \& \& \&  \& $$
\infty_{0}
$$ \&  \&  \& \& <br>

\hline $2.00 \mathrm{E}+00$ \& 2.29E+04 \& -1.31E+04 \& $280 E+03$ \& 1.40E+03 \& \& 1.70E+03 \& 3.31E-04 \& $2.77 \mathrm{E}-04$ \& \& \& \& \& \& \& \& <br>
\hline $1.59 E+00$ \& 2.50E+04 \& -1.38E+04 \& 2.83E+03 \& 1.57E+03 \& \& 201 E 03 \& 3 09E-04 \& 2.41 E-04 \& \& \& \& \& \& \& \& <br>
\hline 1.28E 00 \& $2.71 \mathrm{E}+04$ \& -1.45E+04 \& 3.07E+03 \& 1.64E+03 \& \& 2 25E403 \& 2 90E-04 \& 2.12E-04 \& \& \& \& \& \& \& \& <br>
\hline 1.00E+00 \& $204 \mathrm{E}+04$ \& -1.49E+04 \& 3 ME+03 \& 1.60E+03 \& \& $2.52 \mathrm{E}+03$ \& $2.73 \mathrm{E}-04$ \& 1.84E-a4 \& \& \& \& \& \& \& \& <br>
\hline $7.98 \mathrm{E}-01$ \& 3.15E+04 \& -1.56E+04 \& $357 \mathrm{E}+03$ \& 1.7TE+03 \& \& 2.75E+03 \& 2.57E-04 \& 1.05E-04 \& \& \& \& \& \& \& \& <br>
\hline 6 32E-01 \& 3 38E+04 \& -1.62E+04 \& 3 23E+03 \& 1.84E+03 \& \& $301 \mathrm{E}+03$ \& $242 \mathrm{E}-04$ \& $147 E-04$ \& \& \& \& \& \& \& \& <br>
\hline 5 02E-01 \& $363 \mathrm{E}+04$ \& -1.67E+04 \& $412 \mathrm{E}+03$ \& $189 E+03$ \& \& 3 30E+03 \& 2.28E-04 \& 1.31E-04 \& \& \& \& \& \& \& \& <br>
\hline 3.99E-01 \& $383 \mathrm{E}+04$ \& -1.78E+04 \& 4.34E+03 \& $1.99 \mathrm{E}+03$ \& \& 3.52E+03 \& $2.15 E-04$ \& $1.22 \mathrm{E}-04$ \& \& \& \& \& \& \& \& <br>
\hline 3 17E-01 \& 4.09E+04 \& -1 85E+04 \& 484E+03 \& $2.10 E+03$ \& \& $382 \mathrm{E}+03$ \& $201 E-04$ \& 1.10E-04 \& \& \& \& \& \& \& \& <br>
\hline $2.52 \mathrm{E}-01$ \& 4.33E+04 \& -191E+04 \& 4 91E+03 \& $2.17 \mathrm{E}+03$ \& \& $4.09 E+03$ \& 1.91E-04 \& 1.01E-04 \& \& \& \& \& \& \& \& <br>
\hline 2 00E-09 \& 4.50E+04 \& -200E+04 \& 3.20E+03 \& 2.27E+03 \& \& $4.38 \mathrm{E}+03$ \& 1.80E-04 \& - 32E-03 \& \& \& \& \& \& \& \& <br>
\hline $1.50 \mathrm{E} \cdot 01$ \& 4 90E+04 \& -2.13E+04 \& 5.56E+03 \& 2.42E+03 \& \& $4.74 E+03$ \& 1.87E-04 \& 35E-05 \& \& \& \& \& \& \& \& <br>
\hline 1.28E-01 \& 5.18E+04 \& $231 E+04$ \& $588 \mathrm{E}+03$ \& $2.62 \mathrm{E}+03$ \& \& $508 E+03$ \& 1 50E-04 \& 108E-05 \& \& \& \& \& \& \& \& <br>
\hline 1.00E-01 \& $552 \mathrm{E}+0$ \& 2.51E+ \& $6.26 E+03$ \& $285 \mathrm{E}+03$ \& \& 5.44E+03 \& 1.44E-04 \& 7.55E-05 \& \& \& \& \& \& \& \& <br>
\hline
\end{tabular}






 $150 E+\infty 86161 E+03894 E+01750 E+02=74 E+\infty 0$ $\begin{array}{llll}100 E+03 & 606 E E+03 & -1 \\ -1 & 13 E+02 & 752 E+02 & 6.5 E E+\infty \\ 754 E+02 & 196 E+01\end{array}$ $706 E+02887 E+03-292 E+02757 E+02 \quad 332 \mathrm{E}+01$




 $159 E+02713 \mathrm{E}+03-1.57 \mathrm{~F}+038$ 08E+02 $178 \mathrm{EE}+02$ $\begin{array}{llll}1.200 E+02 & 7.20 E+03 & -1 & 88 E+03 \\ 7425+03 & -2 & 25 E+05 & 23 E+02 \\ 1 & 21 E+02 & 213 E+02 \\ 255 E+02\end{array}$ $796 E+01761 E+03-268 E+03863 E+02304 E+02$ $\begin{array}{llll}832 E+0178 E E+03 & 3.18 E+03 ~ & 1091 E+02 & 3.61 E+02\end{array}$


 $\begin{array}{llll}252 E+01 & 50 E+03 & -110 E+03 & 1.00 E+03 \\ 2.00 E+01 & 1.02 E+04 & 702 E+02\end{array}$ $159 E+01$ 1.002 0 +04 7 24E $+03115 E+038$ 821E+02 $126 E+01$ i. 19EE+04 9 43E+03 $1.24 E+03$ o $56 E+02$ $7.98 E+\infty 01$ 1 $30 E+04-113 E+041.47 E+\infty 3 \quad 1.28 E+\infty 9$ ( $32 \mathrm{E}+00$ 1.58E+04 -1.31E+04 1 62E+03 $148 \mathrm{C}+03$ | 5 | $52 E+\infty$ | $1.78 E+04$ | -1 | $50 E+04$ |
| :--- | :--- | :--- | :--- | :--- |
|  | $1.70 E+03$ | $1.70 E+\infty$ |  |  |






 | $1.00 E+\infty 0$ | 3 | $99 E+04$ | $-4.18 E+04$ |
| :--- | :--- | :--- | :--- |
| 7 | $453 E+03$ | $4.20 E+03$ |  |







 $\begin{array}{lllll} & \text { OOE-01 } & 135 E+05 & -1.39 E+06 & 1.36 E+04 \\ 1.53 E+04 & 138 E+0 \\ 157 E+0\end{array}$
$\begin{array}{lllllll}2000+03 & 7.21 E+\infty & 1 & 00 E+02 & 17 E+02 & -182 E+01 & \text { 2 } 22 E+00\end{array}$
 $1.00 E+03731 E+03-207 E+02: 29 E+02 \quad 2.35 E+01$ $796 \mathrm{E}+027.35 \mathrm{E}+03 \mathrm{3} 318 \mathrm{E}+02 \mathrm{a}$ 2.34E+02 3 300E+01

 \begin{tabular}{llll}
$502 E+02$ \& $746 E+03$ \& $-.39 E+02$ \& $8.46 E+02$ <br>
\hline \& . $115 \mathrm{E}+01$

 

$3.99 E+022$ \& $7.53 E+03$ \& -6 <br>
$3.04 E+02$ \& $854 E+02$ \& $7.53 E+01$ <br>
$3.17 E+022$ \& $761 E+03$ \& $-7.90 E+02$ \& $8.63 E+02$ <br>
\hline
\end{tabular}

 $2.00 E+02 \quad 7.00 \mathrm{E}+03 \mathrm{-1.12E+03}$ : $14 \mathrm{E}+02 \quad 127 \mathrm{E}+02$ $1.59 E+027.91 E+03$-1 $31 E+00$ a $97 E+028148 E+02$ 1.28E +02 : OUE $+03-1.53 \mathrm{E}+03 \mathrm{~B}, 12 \mathrm{E}+02$ OOE+02 $120 E+03-1.78 E+039.203 E+02$ $\begin{array}{llll}0.32 E+01 & 6.58 E+03 & 2.43 E+03 & 9.73 E+022\end{array}$ $502 E+01888 E+033$-2.03E+03 1.01E+03 $2.76 E+02$
 $\begin{array}{lllll}1.17 E+01 & 9.40 E+03 & -3.37 E+\infty 3 & 1.03 E+03 & 3.78 E+02 \\ 1.07 E+03 & 4.005+02\end{array}$ $\begin{array}{lllll}2.52 E+01 & 100 E+03 \\ 200 E+09 & -1.52 E+00 & 1.12 E+03 & 5.13 E+02\end{array}$

 1.00E+01 1.20E+04 -7 OCE +03 1.46E $+\infty 3$ OOSE+02 $7.80 E+\infty 1.40 E+04+0.03 E+091.5 S E+03102 E+00$

 $317 E+00205 E+04-1.36 E+04232 \mathrm{E}+03 \mathrm{I}$ 1.54E+03 2.52E+00 $2.25 E+04-1.47 E+04 \quad 2.55 E+0316 E E+03$




 32E-01 3.78E+04 -2 16E404 4.20E+03 2.45E403 $502 E-014.12 \mathrm{E}+04-2.27 \mathrm{E}+04407 \mathrm{EF}+03 \quad 257 \mathrm{E}+03$ 90E-01 4.38E+04 -2 46E+04 4.97E+03 2.78E+03 | $3.52 E-01$ | $500 E+04$ | $-2.82 E+04$ | $6,74 E+00$ | $200 E+03$ |
| :--- | :--- | :--- | :--- | :--- |

 $50 E-01888 E+04-323 E+04$ C.67E $+03306 E+03$ 28E-01 $635 E+04-363 E+04 \quad 7.20 \mathrm{E}+03401 \mathrm{E} 403$ (.00)


































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