

KINETIC AND THERMOCHEMICAL STUDIES OF
RHENIUM-HALOGEN COMPOUNDS

A thesis presented for the Degree of
Doctor of Philosophy, in the
Faculty of Science, University of Leicester,
by S. J. Cartwright

October 1975

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STATEMENT

The work described in this thesis was carried out by the author in the Department of Chemistry of the University of Leicester between October 1972 and September 1975.

No part of this work has been submitted or is concurrently being submitted for any other degree.

Signed

A handwritten signature in cursive script, appearing to read 'S. J. Cartwright', written over a horizontal line.

October 1975

S. J. Cartwright

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I wish to extend my most sincere thanks to Dr. J. Burgess for his continual help and guidance throughout this work, for his unstinting enthusiasm and for his willingness to discuss any problems that arose.

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CHAPTER 1

GENERAL INTRODUCTION

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GENERAL INTRODUCTION

Rhenium, a third row transition element, forms compounds with all of the halogens (both binary and complex halides) in a variety of oxidation states. The chemistry of these compounds has previously been described in standard texts on rhenium,^{1,2} and this thesis is concerned with further extending the knowledge of the chemistry of several of these rhenium halides.

Rhenium burns in fluorine, giving a mixture of the hexa- and heptafluorides. It combines readily with chlorine and bromine, but does not react appreciably with iodine. As in the cases of other transition metals, there has been a great deal of interest and research in the last two decades in the simple halides and oxide halides of rhenium. Rhenium-fluorine chemistry is extensive, despite the fact that there are no compounds in which the oxidation state of the metal is less than +4. Three binary chlorides of rhenium are known, the trichloride, tetrachloride and pentachloride, while there is still some controversy over the evidence for the existence of a fourth binary chloride, rhenium hexachloride. The complex halides of rhenium exist with the metal in the oxidation states, 3, 4, 5 and 6. The structural and physical properties of the quadrivalent salts have been studied extensively, both because of the electronic configuration of the octahedral rhenium(IV) entity, d^3 , and the ease of

handling the compounds. Less is known of the thermochemical properties. Organometallic derivatives and carbonyls, such as the rhenium pentacarbonyl halides where the metal is in an oxidation state of +1 and has a low-spin d^6 electronic configuration, represent one of the most rapidly advancing fields of rhenium chemistry. The resemblance between manganese, technetium and rhenium is closest in these low valency compounds.

The alkaline hydrolyses of all halides and complex halides of rhenium follow a well defined pattern. A compound of rhenium(VII) always hydrolyses to perrhenate ion (tetraoxorhenate(VII)) and no precipitate appears. Compounds of rhenium(VI) and rhenium(V) always disproportionate into rhenium(IV) and rhenium(VII). The fraction appearing as rhenium(IV) is always obtained as the insoluble hydrated dioxide, which can be separated from the soluble perrhenate. Compounds of rhenium(IV) hydrolyse to give all the rhenium as the dioxide. This type of behaviour is of wide application and is used frequently in the thermochemical studies detailed in Chapter 2.

The objectives of this chapter are to describe briefly recent advances in the thermochemical and kinetic studies of the halogen chemistry of rhenium and to outline the arrangement of this thesis. The work herein falls into two general categories, thermochemistry and reaction kinetics. In the last few years much effort has gone into the study of the thermochemistry of the halides of the refractory metals, molybdenum and tungsten.³ However, not much thermochemical study has been devoted to the halides, both binary and

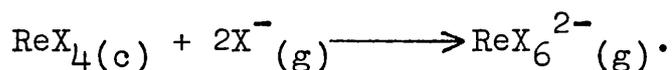
complex, of rhenium. The thermochemical work that has been done on rhenium halides has centred around the rhenium-chlorine system and the hexachlororhenate(IV) anion is probably the best known and most studied complex of rhenium.

Busey et al have measured the enthalpy of solution of potassium hexachlororhenate(IV) in 0.0100 molar hydrochloric acid solution as a function of concentration, using a solution calorimeter consisting of a Dewar flask and a copper resistance thermometer.^{4,5} Extrapolation to infinite dilution gave a standard enthalpy of solution at 298.2K of $10.397 \text{ kcal mol}^{-1}$ ($43.501 \text{ kJ mol}^{-1}$). From this result and the known solubility of the salt, the entropy of ReCl_6^{2-} (aq) was calculated to be $59.5 \pm 0.04 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ($248.9 \pm 1.7 \text{ J K}^{-1} \text{ mol}^{-1}$). In a later paper,⁶ Busey et al. calorimetrically measured the enthalpy of oxidative hydrolysis of crystalline potassium hexachlororhenate(IV), by alkaline hypochlorite solution, as $-152.7 \pm 0.6 \text{ kcal mol}^{-1}$ ($-638.9 \pm 2.5 \text{ kJ mol}^{-1}$) at 298.2K. Complementing this, the enthalpy of alkaline hydrolysis of potassium hexachlororhenate(IV) was observed to be $-63.6 \pm 0.2 \text{ kcal mol}^{-1}$ ($-266.1 \pm 0.8 \text{ kJ mol}^{-1}$). From the above enthalpy of oxidative hydrolysis and other thermodynamic data, the authors arrived at values of -183.0 and $-141.6 \text{ kcal mol}^{-1}$ (-765.7 and $-592.5 \text{ kJ mol}^{-1}$) for the enthalpy and free energy of formation of ReCl_6^{2-} (aq) respectively. Peacock et al.⁷ estimated an enthalpy of formation of crystalline rhenium pentachloride of $-86.1 \pm 0.8 \text{ kcal mol}^{-1}$ ($-360.2 \pm 3.3 \text{ kJ mol}^{-1}$) from hydrolysis measurements. Precise thermochemical data are also available for rhenium trichloride⁸ and tribromide.⁹

Considering the similarities between the rhenium-chlorine and rhenium-bromine systems, it is surprising that little study has been made of the thermochemistry of the rhenium-bromine system. Chapter 2 deals with specific thermochemical studies of both systems. The rhenium-fluorine system has not been included because of the difficulties encountered in preparing K_2ReF_6 free of such salts as K_2ReF_5OH . Moreover, the salts of hexafluororhenate(IV) are not easily attacked by alkalis.² As far as the rhenium-iodine system is concerned, it is extremely difficult to prepare the hexaiodorhenate(IV) salts free from hydrolysis and redox products,¹⁰ and rhenium tetraiodide is rather unstable, loses iodine slowly in a vacuum at room temperature and is extremely hygroscopic.¹¹

Chapter 2 deals specifically with the thermochemistry of the compounds, potassium hexachloro- and hexabromorhenate(IV), β -rhenium tetrachloride, rhenium tetrabromide and rhenium oxide tetrachloride. The standard enthalpies of formation of these compounds have been determined indirectly via the experimental measurement of their enthalpies of hydrolysis (alkaline or oxidative). This method is particularly useful because the equations of the hydrolyses are well established and the rhenium is converted quantitatively into the perrhenate anion or the hydrated rhenium dioxide precipitate. The crystal structures of the two potassium salts are fully characterised¹² and the crystal data have been used in the simple Born-Mayer equation¹³ to obtain an estimate of the lattice energies of the respective salts. The standard enthalpies of formation of $K_2ReX_6(c)$ and $ReX_4(c)$ and the lattice enthalpy of K_2ReX_6 have been

used in a Born-Haber thermochemical cycle to obtain an estimate for the enthalpy, ΔH_{2X^-} , of the reaction,



The enthalpy estimates for $\beta\text{-ReCl}_4$ and ReBr_4 , $\Delta H_{2\text{Cl}^-}$ and $\Delta H_{2\text{Br}^-}$ respectively, reflect the ability of the tetrahalide to accept halide ions, i.e. the Lewis acidity of the tetrahalide. The Lewis acidities of $\beta\text{-ReCl}_4$ and ReBr_4 have been compared with those of the tetrahalides of other transition metals and of main group metals.

Little is known of the thermodynamics of solvation of halo- anions in general and even less about hexahalorhenate(IV) anions in particular. The caesium salts of hexachlororhenate(IV) and hexabromorhenate(IV) have well characterised antiferro structures and good estimates of their lattice energies can thus be made. Moreover, the two salts are sparingly soluble in aqueous solution and so their solubility products can be determined quite accurately without the ancillary determination of activity coefficients. Both caesium salts have low solubilities in water and the anions have well defined absorption bands in the ultra-violet region of the electromagnetic spectrum. In addition, unlike many other halo- anions of transition metals, hexachlororhenate(IV) and hexabromorhenate(IV) anions, where the rhenium entity has a kinetically inert d^3 electronic configuration, are sufficiently long-lived in solution for measurements of solubilities to be made. Chapter 3 deals with the solubility of the caesium salts of the hexachlororhenate(IV) and hexabromorhenate(IV) anions, firstly in water and secondly in mixed aqueous solvents.

The concentrations of both anions in water have been measured spectrophotometrically over a range of temperatures and the solubility products of the salts have thence been calculated. From the variation of solubility products of these salts with temperature, values for the enthalpies of solution have been determined, assuming that the activity coefficients are invariant with temperature. The caesium salts of hexachlororhenate(IV) and hexabromorhenate(IV), like the corresponding potassium and rubidium salts, crystallise in an antiferite (K_2PtCl_6) lattice.¹⁴ The lattice energies of the caesium salts have been calculated, again by the use of the Born-Mayer equation. A thermochemical cycle has been used in this chapter, along with values for the enthalpies of solution and for the lattice enthalpies of the caesium salts, to obtain estimates of the hydration enthalpies of the salts. Use has been made of Halliwell and Nyburg's¹⁵ value for the hydration enthalpy of the proton, $-1091 \pm 10.5 \text{ kJ mol}^{-1}$, to split the hydration enthalpies of the caesium salts into single-ion values. Single-ion estimates for other hexahaloanions have been determined in a similar way from published solubility data and known crystal structures. The single-ion values for $ReCl_6^{2-}$ and $ReBr_6^{2-}$ have been linked to the previously published value for SO_4^{2-} ¹⁶ by the estimation of the single-ion hydration enthalpy of ReO_4^- , for which solubility and crystal data are available. A comparison of the single-ion values thus determined has been made and their variation has been linked to the estimated anionic radii.

The second part of Chapter 3 deals with the solubility of caesium hexachlororhenate(IV) in several water-rich, mixed aqueous solvents, and an attempt has been made to correlate the solubility product of the salt with various empirical solvent parameters. The Gibbs free energy of transfer of ReCl_6^{2-} , $\delta_{\text{m}}\mu^\ominus(\text{ReCl}_6^{2-})$, has been studied, upon transfer from water to the various mixed aqueous solvents.

There have been few kinetic studies of substitution in rhenium complexes in solution. Kinetic studies of substitution in rhenium(IV) complexes have been limited until recently to those of chloride ion exchange with hexachlororhenate(IV)¹⁷ and bromide exchange with hexabromorhenate(IV)¹⁸ ions in aqueous solution, and of ligand exchange in solid K_2ReCl_6 and K_2ReBr_6 .¹⁹ More recently, Burgess et al. have studied the aquation of the hexabromorhenate(IV) anion in aqueous and aqueous-organic media and the mercury(II) catalysed aquation of the hexachlororhenate(IV) anion in aqueous solution.²⁰ It is rather surprising that, up to the time of the work by Burgess et al, so few kinetic studies of substitution in rhenium(IV) had been made, for the ion is a kinetically inert d^3 centre which should be amenable to study by conventional techniques, like the extensively investigated chromium(III)²¹ and the less extensively studied vanadium(II)²² d^3 centres.

The work reported in Chapter 4 follows on from the work by Burgess et al. The investigation has been restricted to the kinetics of aquation of hexachlororhenate(IV) and hexabromorhenate(IV) anions because the aquation of the hexafluororhenate(IV) anion is inconveniently slow and the

rapid aquation of the hexaiodorhenate(IV) anion presents grave technical problems. (Iodine will attack the steel of a stopped-flow apparatus and the presence of iodide makes spectrophotometric observations difficult.) Moreover, for any kinetic study on the aquation of hexaiodorhenate(IV), the presence of iodide ion might disturb the system by the formation of rhenium(III)-iodide complexes.

The aquation of ReX_6^{2-} anions involves substitution at ReX_6^{2-} accompanied by oxidation to ReO_4^- . The rate of reaction can be followed spectrophotometrically because of the well defined absorption maxima in the ultra-violet spectra of aqueous solutions of both ReCl_6^{2-} and ReBr_6^{2-} . An extensive study has been made of the metal-ion (Hg^{2+} , Tl^{3+} , In^{3+} and Cd^{2+}) catalysed aquation of the hexachlororhenate(IV) anion in aqueous solution. Activation parameters have been determined for the most effectively catalysed aquations. The study of the metal-ion catalysed aquation of the hexabromorhenate(IV) anion has been restricted to the thallium(III) catalysed reaction because of the precipitation that occurred when hexabromorhenate(IV) and mercury(II) solutions were mixed. A rate law has been proposed to explain the observations and rate constants have been quoted for all the catalysed aquations for at least one temperature. The results have been compared with data available on similar systems and the catalytic activity of the various metal-ions has been linked to the stability constants for the monohalo-complexes of the respective metal-ions.

Substitution at complexes of rhenium(I) are also amenable to kinetic study because of the kinetically inert low-spin d^6 configuration of the rhenium. The most likely place to look for complexes of rhenium(I) is amongst carbonyls and other organometallic compounds. There is a great deal of chemistry known on the substitution reactions of manganese and rhenium pentacarbonyl halides. Available kinetic data on the substitution reactions of manganese pentacarbonyl halides are extensive,^{23,24} but few are available on the substitution reactions of rhenium pentacarbonyl halides.

Chapter 5 deals with the kinetics of the reactions of rhenium pentacarbonyl chloride, bromide and iodide with an excess of cyanide ion in aqueous methanolic solution. The reactions of all three halides follow a kinetic pattern of two consecutive first order steps with the formation of a common product, $[\text{Re}(\text{CO})_4(\text{CN})_2]^-$. Rate laws have been determined, for both steps of the reaction of each halide, and rate constants have been measured. It is possible to follow the reaction of rhenium pentacarbonyl iodide with excess of cyanide at various temperatures, and activation parameters have been calculated. The change from a purely associative mechanism, for the first step of the reaction of all three rhenium pentacarbonyl halides, to a partly dissociative mechanism (for the iodide) or predominantly dissociative mechanism (for the chloride and bromide), for the second step, has been discussed. The change in the rate of the reaction of rhenium pentacarbonyl iodide with excess of cyanide, upon change of solvent medium, has been examined in terms of the Gibbs free energy of transfer of rhenium

pentacarbonyl iodide, $\delta_m \mu^\ominus[\text{Re}(\text{CO})_5\text{I}]$. The transfer parameter has been estimated from solubility measurements in the appropriate solvent media.

In summary, the aim of the following chapters is to extend the knowledge of the thermochemistry of known halides of rhenium, in order that the chemical reactions and stability of rhenium halides may be more fully understood, and to expand the present data on the kinetics of the substitution reactions of rhenium-halide complexes in solution.

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CHAPTER 2

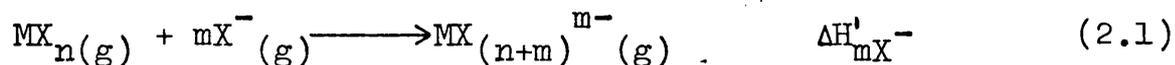
THERMOCHEMICAL PROPERTIES OF
SOME RHENIUM HALIDES

CHAPTER 2THERMOCHEMICAL PROPERTIES OF
SOME RHENIUM HALIDESINTRODUCTION

To understand chemical processes it is necessary to understand the energetics of the systems involved. Thermochemistry is a study of the determination and application of these energetics.

An important part of thermochemistry involves the determination of enthalpies of formation. Over the last twenty years much work has been done on the thermochemistry of some halides of the refractory metals, particularly those of molybdenum and tungsten. Less thermochemical data are known of the halides of rhenium. The aim of this present study is to extend the knowledge of the thermochemistry of some chlorides and bromides of rhenium.

Lewis acidities (equation (2.1)) of binary halides are of interest to the synthetic chemist in connection with the prediction of new syntheses for known compounds and the possible existence and reactions of unknown compounds. Not much thermochemical data are available for complex chlorides and bromides. The enthalpy change this work is concerned with is the formation of a bond between a halide ion acceptor (Lewis acid) and the halide ion.

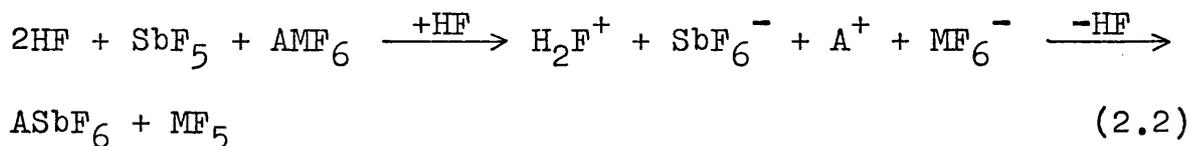


$\Delta H_{m\text{X}^-}^{\text{I}}$ may be referred to as the Lewis acidity of the species MX_n . (M is a metal-ion, X^- is a halide ion and $m\text{X}^-$ refers to the number of halide ions added to MX_n in the reaction.)

Although free energy data are the final requirement in complete thermodynamic calculation of stability, measurements have been confined to changes in enthalpy. It has been argued that enthalpies of reaction can give some idea of the strength of donor-acceptor interaction,¹ and certainly among closely related molecules, where the change in entropy is likely to be fairly constant, the enthalpy of reaction will parallel the free energy change. Hence, if the enthalpy of the reaction shown in equation (2.1) is large and negative, then $\text{MX}_{(n+m)}^{m-}$ may exert a stabilising influence on unusual cations.

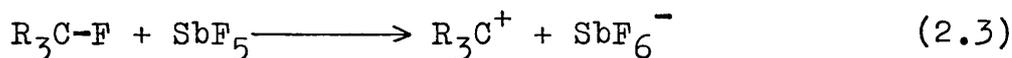
The Lewis acidities of boron trifluoride² and the pentafluorides of antimony,³⁻⁵ arsenic,^{6,7} molybdenum⁶ and phosphorus⁷ in anhydrous hydrogen fluoride have been assessed. Antimony pentafluoride was judged to be the strongest Lewis acid of this group and this observation has been made use of by an ingenious preparation of several transition metal pentafluorides (equation (2.2)). On dissolving a stoichiometric quantity of antimony pentafluoride in anhydrous hydrogen fluoride containing an alkali metal hexafluorometallate(V), the two Lewis acids compete for the decreasing concentration of fluoride ions as the solvent is removed. Since antimony pentafluoride is the stronger Lewis acid (fluoride ion acceptor), the hexafluoroantimonate(V)

anion is formed preferentially, and the pure transition metal pentafluoride may be removed from the reaction vessel by sublimation.

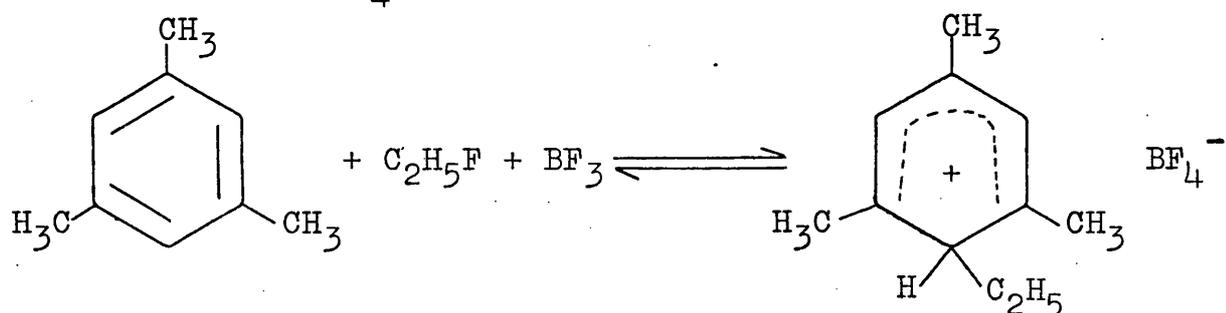


(A = Na, K, Rb, Cs; M = Nb, Mo, W)

In the field of organic chemistry, Olah⁸ has used the strong Lewis acidity of certain species to catalyse electrophilic aromatic substitutions. Olah and other workers have used Lewis acids such as boron trifluoride, aluminium chloride, iron(III) chloride, zinc chloride, proton and titanium tetrachloride in the acetylation, halogenation and benzylation of toluene and benzene. For example, the use of antimony pentafluoride with propyl, butyl or pentyl fluoride produces a stable carbonium ion,⁹



Olah⁸ has similarly used boron trifluoride with ethyl fluoride, in the presence of aromatic compounds, to produce the C_2H_5^+ carbonium ion which then undergoes electrophilic aromatic substitution at the aromatic compound to form arenium ions. These arenium ions are stabilised by the presence of the BF_4^- anion. For example,



(2.4)

The production and stabilisation of such carbonium ions are obviously of interest because of the range of compounds thus made readily available. Such reactions as hydrolysis, alcoholysis, ester formation, S- and N- alkylation, carbonylation, aromatic alkylation, etc. are more straightforward because of the formation and stabilisation of alkyl carbonium ions from the reaction of alkyl fluorides with antimony pentafluoride.

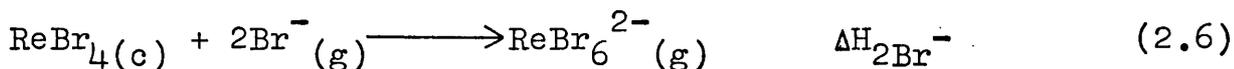
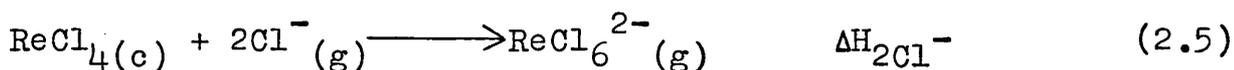
One is obviously interested in the possibility of finding other strong Lewis acids to accept chloride or bromide ions and thus produce unusual cations that will be stabilised in the presence of the halometallate anions. It was with this idea in mind that the Lewis acidities of a few binary rhenium halides were examined and compared with values for several other binary metal halides.

Both potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV) adopt the antiferite structure (K_2PtCl_6), with four molecules per unit cell, and are green and red crystalline solids respectively. Rhenium tetrachloride is said to exist in three forms, α ,¹⁰ β ¹⁰ and γ .¹¹ β -Rhenium tetrachloride, which is very much better attested to than the α form and was used in the present study, is a dimeric black or dark purple crystalline solid, stable indefinitely in a vacuum at room temperature. Rhenium tetrabromide is a deep red solid.¹² Rhenium pentachloride forms a deep brown or black solid melting at 493K.¹² Rhenium oxide tetrachloride forms a brownish crystalline solid which melts at 303K to give a brown liquid.¹² These compounds were suitable for thermochemical study and yielded

estimates of the Lewis acidities of β -rhenium tetrachloride and rhenium tetrabromide.

There are two main methods used to determine enthalpies of formation, direct methods and indirect methods. Direct methods involve the direct combination of or dissociation into the elements concerned. Indirect methods make use of Hess's Law of Constant Heat Summation,¹³ which, in its simplest form, states that the overall change in enthalpy or energy of a chemical reaction is independent of the path, that is, independent of any intermediate reactions that may occur. The indirect method applied in the present work uses the experimental determination of enthalpies of hydrolysis to derive standard enthalpies of formation.

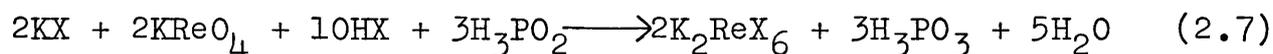
The derived standard enthalpies of formation have been used in the study of the interaction between element halide Lewis acids and Lewis bases. Ideally, one should determine the enthalpy change for a gas phase reaction, but only in rare favourable cases is this possible. Results on the Lewis acidity of crystalline β -rhenium tetrachloride and rhenium tetrabromide (equations (2.5) and (2.6) respectively) are reported herein.



These enthalpy changes are compared with those for similar tetrahalides and various reactivity trends are discussed.

EXPERIMENTALPreparation of Compounds

Potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV) were prepared by reducing solutions of potassium perrhenate in the appropriate concentrated hydrohalic acid with hypophosphorous acid.¹⁴ The complexes were then recrystallised from the relevant concentrated hydrohalic acid, washed with acetone, then ether, and were finally air dried.

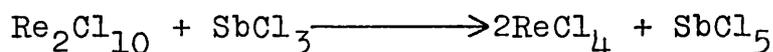
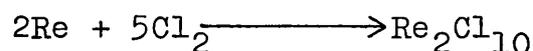
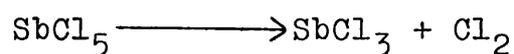


The analogous rubidium and caesium salts were prepared by dissolving the potassium salt in the relevant concentrated hydrohalic acid and adding the necessary rubidium or caesium halide dissolved in dilute acid. Each of the rubidium and caesium salts thus precipitated out of the concentrated acid solutions was washed in the same manner as the potassium salts.

Rhenium pentachloride was prepared by the direct combustion of metallic rhenium in a current of dry chlorine at a temperature of about 673K.¹⁵ Purification was achieved by distilling off the rhenium oxide tetrachloride impurity at 323K, followed by distillation of the product at 433K, both in a current of dry chlorine. The distilled product was sealed in a pyrex tube under dynamic vacuum and transferred to a dry-box for further handling.

β -Rhenium tetrachloride was prepared by two methods.¹⁶

One method involved the reaction of powdered rhenium metal and antimony pentachloride (molar ratio Re:SbCl₅ of 1:2.5) in a sealed, evacuated, silica Carius tube (constricted in the middle so that it was composed of two sections) at a temperature of 873K for 48 hours. Purification was achieved by transferring the crude product to a test tube (in a dry-box), attaching it to a vacuum line and maintaining a dynamic vacuum at 433K for 48 hours. The impurities (mainly excess of antimony chlorides) distilled off and condensed at a cold spot in the vacuum line. The authors' suggested reaction path is,

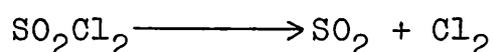


The second method involved the reaction of equimolar quantities of rhenium pentachloride and antimony trichloride in a sealed, evacuated, pyrex Carius tube (again constricted) at a temperature of 573K for 48 hours. The resulting black product was purified in the same manner as in the previous method. The authors' suggested mechanism of formation appears to be a simple reduction,

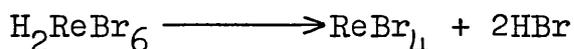
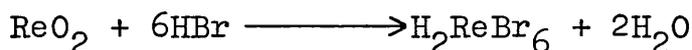


The purified products from both methods were sealed in pyrex tubes under vacuum and transferred to a dry-box for further handling.

Pure rhenium oxide tetrachloride was made quantitatively by the reaction of powdered rhenium metal with an eight-fold excess of sulphuryl chloride in a sealed, evacuated, pyrex Carius tube at about 573K for 72 hours.¹⁷ The excess of sulphuryl chloride was vacuum distilled off at 273K and the brown crystalline product was sealed in an evacuated, pyrex tube and transferred to a dry-box for further handling. The authors' suggested mechanism is:



Rhenium tetrabromide was prepared by the dissolution of rhenium dioxide in concentrated hydrobromic acid, followed by evaporation down to a small volume.¹⁸ The concentrated solution was then dried in a desiccator over KOH/P₂O₅.



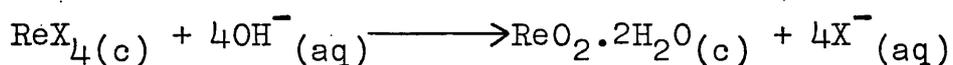
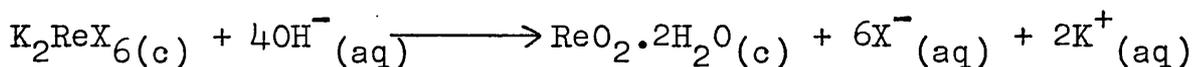
Analysis

See Appendix 2.

Hydrolysis of Rhenium Halides

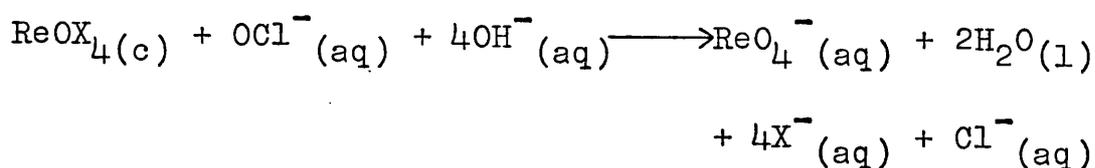
It is possible to perform hydrolyses (either alkaline or oxidative) on various soluble rhenium halides and measure

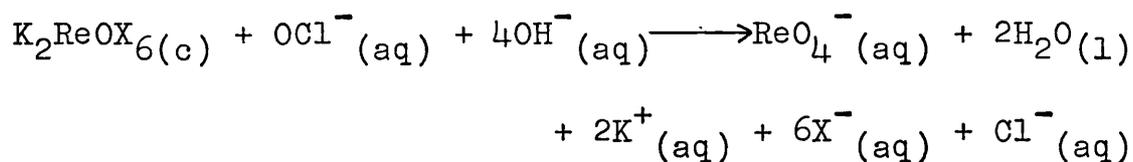
the enthalpy change. For the compounds where rhenium is in an oxidation state of +4, it is convenient to perform alkaline hydrolysis whereupon the rhenium is quantitatively precipitated out of solution as the black hydrated dioxide, $\text{ReO}_2 \cdot 2\text{H}_2\text{O}$.¹⁹ For example,



Due to the chemical observation¹⁹ that freshly precipitated rhenium dioxide is much more readily oxidised than the 'aged' dioxide in hydroxide solution, the thermodynamic properties of the two dioxides differ. In the present work, precipitation of rhenium dioxide out of anaerobic hydroxide solution was always performed under the same conditions. (Anaerobic conditions were required to minimise oxidation of $\text{ReO}_2 \cdot 2\text{H}_2\text{O}$ to ReO_4^- by dissolved oxygen.) Since all the thermochemical measurements were taken for the formation of freshly precipitated dioxide, the standard enthalpy of formation of rhenium dioxide used is that quoted by Busey et al.,¹⁹ $-241.8 \pm 1.5 \text{ kcal mol}^{-1}$ ($-1011.7 \pm 6.3 \text{ kJ mol}^{-1}$).

For compounds where rhenium is in other oxidation states, it is more convenient to perform oxidative hydrolysis by the use of basic hypochlorite solutions. In these cases, the rhenium is quantitatively converted to the colourless perrhenate anion, ReO_4^- .²⁰ For example,



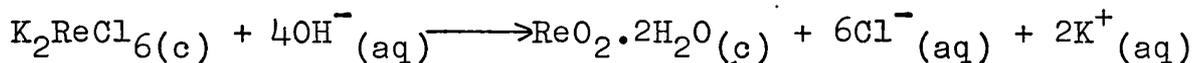


It is thus very convenient to measure the enthalpy change of such reactions, where $\text{ReO}_2 \cdot 2\text{H}_2\text{O}$ or ReO_4^- are generated, because the generation of these two species is well characterised, the species are easy to generate quantitatively, and their standard enthalpies of formation are well established.

Appendix 1 deals with the calorimetric procedure for a typical hydrolysis, the apparatus, the measurement of the enthalpy change and the calibration of the equipment.

Treatment of Results

For each compound, two or more discrete samples were prepared and enthalpies of hydrolysis were experimentally measured at 298.2K for each sample. From the experimentally determined enthalpies of hydrolysis and a knowledge of the appropriate stoichiometric equation of the hydrolysis, the standard enthalpies of formation of potassium hexachlororhenate(IV), potassium hexabromorhenate(IV), β -rhenium tetrachloride, rhenium tetrabromide and rhenium oxide tetrachloride were derived. A typical example of such a calculation is given below for the alkaline hydrolysis of potassium hexachlororhenate(IV).



$$\Delta H_{\text{hydrol.}} = -264.0 \pm 5.4 \text{ kJ mol}^{-1} \text{ ‡}$$

If $\Delta H_{\text{hydrol.}}$ is the mean enthalpy of hydrolysis of potassium hexachlororhenate(IV) and $\Delta H_f^\ominus(\text{OH}^-(\text{aq}))$, $\Delta H_f^\ominus(\text{ReO}_2 \cdot 2\text{H}_2\text{O}(\text{c}))$, $\Delta H_f^\ominus(\text{Cl}^-(\text{aq}))$ and $\Delta H_f^\ominus(\text{K}^+(\text{aq}))$ are the standard enthalpies of formation of $\text{OH}^-(\text{aq})$, $\text{ReO}_2 \cdot 2\text{H}_2\text{O}(\text{c})$, $\text{Cl}^-(\text{aq})$ and $\text{K}^+(\text{aq})$ respectively, the standard enthalpy of formation of crystalline potassium hexachlororhenate(IV), $\Delta H_f^\ominus(\text{K}_2\text{ReCl}_6(\text{c}))$, is given by:

$$\begin{aligned} \Delta H_f^\ominus(\text{K}_2\text{ReCl}_6(\text{c})) &= \Delta H_f^\ominus(\text{ReO}_2 \cdot 2\text{H}_2\text{O}(\text{c})) + 6\Delta H_f^\ominus(\text{Cl}^-(\text{aq})) \\ &\quad + 2\Delta H_f^\ominus(\text{K}^+(\text{aq})) - 4\Delta H_f^\ominus(\text{OH}^-(\text{aq})) - \Delta H_{\text{hydrol.}} \end{aligned}$$

Hence, $\Delta H_f^\ominus(\text{K}_2\text{ReCl}_6(\text{c})) = -1333.1 \pm 5.4 \text{ kJ mol}^{-1}$.

RESULTS

The mean values for the enthalpies of alkaline hydrolysis of the appropriate rhenium halides are reported in Tables 2.1 - 2.5. In the determination of an enthalpy, x , a series of n measurements, x_i , of the enthalpy have been taken. The mean value, \bar{x} , is thus given by

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{i=n} x_i$$

‡ The enthalpy of hydrolysis of K_2ReCl_6 in NaOH reported herein agrees well with that obtained by Busey et al.,¹⁹ $-63.6 \text{ kcal mol}^{-1}$ ($-266.1 \text{ kJ mol}^{-1}$), by direct calorimetric measurement of the reaction in a Dewar vessel under anaerobic conditions.

and has been quoted as the enthalpy. A standard deviation, s , given by

$$s^2 = \frac{1}{n} \sum_{i=1}^{i=n} (x_i - \bar{x})^2$$

follows each enthalpy. Also quoted in Tables 2.1 - 2.5 are the standard errors of the means (SEM) and 90% confidence limits. The 90% confidence limits are derived from s via the formula, $s \times t/\sqrt{n}$; i.e. from the usual formula, assuming a Gaussian distribution and using t values specific for 90% confidence limits.²¹

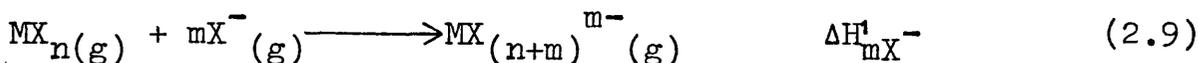
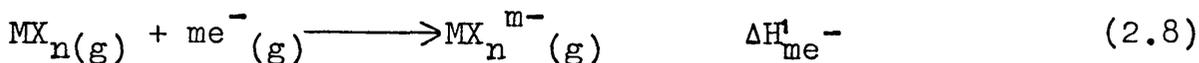
The values for the hydrolysis of the air-stable compounds, potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV), were measured with the more sophisticated LKB calorimetry equipment (Appendix 1). The values obtained for the air-sensitive compounds, β -rhenium tetrachloride, rhenium tetrabromide and rhenium oxide tetrachloride, were measured with the LKB equipment and with the less sophisticated frangible bulb equipment (Appendix 1). Some difficulty was encountered when measuring enthalpies of hydrolysis of the air-sensitive compounds with the LKB equipment. The problem was of accurately weighing the samples into the very small (1 cm³ volume), fragile ampoules in a dry-box.

Consistent values were unobtainable for the enthalpies of hydrolysis of the rubidium and caesium hexahalorhenate(IV) complexes. Both the alkaline and oxidative hydrolyses of these salts were slow and incomplete, leaving undissolved salt after one hour, even in 5 molar sodium hydroxide solution.

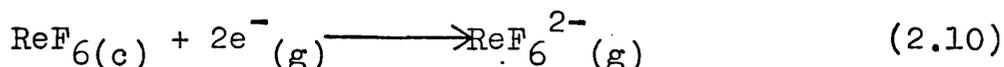
The standard enthalpies of formation of potassium hexabromorhenate(IV), β -rhenium tetrachloride, rhenium tetrabromide and rhenium oxide tetrachloride were calculated in the same manner as previously described for potassium hexachlororhenate(IV). The ancillary thermochemical data required for each calculation are given in Table 2.8, and the derived standard enthalpies of formation of the rhenium halides are reported in Table 2.9.

DISCUSSION

Enthalpies for the reaction of binary halides of molybdenum and tungsten with electrons and with halide ions have been estimated previously²² (equations (2.8) and (2.9)).



The estimates prove useful for comparison with the work herein. Unfortunately, the enthalpy for the reaction of rhenium hexahalides with two electrons can only be estimated for rhenium hexafluoride (equation (2.10)).



The reason for this lies in the fact that rhenium hexabromide and rhenium hexaiodide are unknown (and presumed to be too unstable to exist under normal conditions) and there is a great deal of doubt about the existence of rhenium hexachloride.¹²

It would be difficult to obtain estimates of the enthalpy for the reaction of rhenium tetrahalides with an electron (equation (2.11)), since the trimeric structure of metal tetrahalorhenate(III) salts creates problems in calculating the respective lattice energies.



Moreover, no salts of the tetrabromorhenate(III) anion are yet known to exist; the procedure used to prepare tetrachlororhenate(III) salts (dissolution of rhenium trichloride in hydrochloric acid, followed by precipitation from solution by addition of the appropriate alkali metal chloride), when applied to the preparation of tetrabromorhenate(III) salts, causes the formation of the hexabromorhenate(IV) anion.¹²

As far as the alkali metal salts of the hexahalorhenate(IV) anions are concerned, the hexaiodorhenate(IV) salts have been excluded from the present investigation because they cannot be prepared free from hydrolysis and redox products.²³ It has proved difficult to prepare pure samples of potassium hexafluororhenate(IV) because of the complementary formation of, for example, $\text{K}_2\text{ReF}_5\text{OH}$, during the preparation. It was thus decided to confine the present investigation to the thermochemistry of the more well-documented rhenium-halogen compounds; i.e. the alkali metal salts of the hexachloro- and hexabromorhenate(IV) anions, β -rhenium tetrachloride, rhenium tetrabromide and rhenium oxide tetrachloride.

Lattice Energy Considerations

In the hexahalorhenate(IV) anions, the charges on the central rhenium and on the halide ligands are unknown. One can make certain assumptions about charge distribution and obtain lattice energies (for example, the use of the Born-Mayer equation in the earlier fluoride work reported in Reference 22). From a suitable lattice energy programme, it is possible to calculate coulombic energies by assuming various charge distributions and differing repulsion terms²⁴ (see Tables 2.6 and 2.7). For the purposes of the present discussion, one may assume lattice energy and lattice enthalpy to be synonymous.

Charge distributions can be inferred from lattice energy calculations, either if the crystalline salt has two different phases (for example, K_2MnF_6 has three different crystalline phases, only two of which have been studied), or if one has salts of two different cations with two different phases. Unfortunately, salts of the hexachloro- and hexabromorhenate(IV) anions all have the antiferite crystal lattice. If $BaReCl_6$ were prepared and a standard enthalpy of formation determined, then the lattice energies of K_2ReCl_6 and $BaReCl_6$ could be estimated, in principle, by finding the charge distribution which would give the most consistent fit with the measured standard enthalpies of formation. Even here there may be inconsistencies due to significant changes in charge distribution of the ion from salt to salt. However, it is possible from electronegativity data to calculate likely charge distributions.²⁵ Professor R. D. Peacock has

calculated the various contributions to the lattice energies of potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV) for different charges on the central rhenium and the halide ligands. There are seven models in all for each compound (Tables 2.6 and 2.7). Model V for each compound is based on the charge distributions derived from Jolly's electronegativity equalisation procedure.²⁵

The atomic charges one obtains from Jolly's procedure stand or fall on electronegativity. The numbers have been checked, for simple molecules such as tungsten hexafluoride, against photo-ionisation spectroscopy data and appear to be satisfactory. The relative differences between the final values obtained for the lattice energies from Jolly's method and those from the Born-Mayer²⁶ assumptions are not likely to be important - especially because the charge distribution between metal and halide is likely to be reasonably close. This is illustrated by the 'flattening out' of the nett U_L values for both salts in Tables 2.6 and 2.7, as one moves from model I through to model VII.

With these qualifications in mind, the lattice energies of potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV) were calculated by using the Born-Mayer equation²⁶ (equation 2.12)). The reason for using this equation is to facilitate comparisons with previous work on the Lewis acidities of transition metal binary halides, where all lattice energies were calculated using either the Born-Mayer equation or the Kapustinskii equation²⁷ derived from the former. However, where the lattice energies from Professor Peacock's programme may be more illuminating,

these results will be quoted along with the parameters derived therefrom.

Thermochemical Calculations

The simple Born-Mayer equation is

$$U_L = - \frac{N_0 A |z_1| |z_2| e^2}{r_0} \left(1 - \frac{\rho}{r_0}\right) \quad (2.12)$$

where,

N_0 is the Avogadro number, $6.023 \times 10^{23} \text{ mol}^{-1}$.

A is the Madelung constant; ²⁸ 5.03879 for a regular anti-fluorite lattice.

z_1 and z_2 are the charges of the constituent ions.

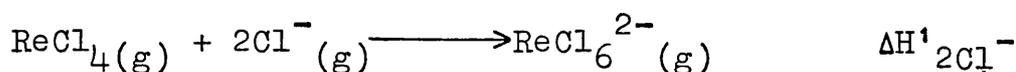
e is the charge on an electron, $1.60210 \times 10^{-19} \text{ C}$.

r_0 is the distance between cation and anion, measured in Å.

ρ is the repulsion term, 0.345 Å .

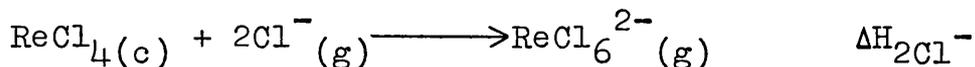
Lattice parameters, calculated r_0 values and calculated lattice enthalpies, ΔH_L , for the two potassium salts are reported in Table 2.10.

Born-Haber thermochemical cycles are a consequence of Hess's Law of Heat Summation. One can use such a thermochemical cycle to estimate the sum of the first and second enthalpy changes for the reaction of gaseous β -rhenium tetrachloride with gaseous chloride ion, i.e.



This enthalpy change is difficult to estimate because β -rhenium tetrachloride is thermally unstable and it is

thus impossible to determine a reasonably accurate value for its enthalpy of sublimation. However, one can still calculate the more thermochemically useful sum of the first and second enthalpy changes for the reaction of crystalline β -rhenium tetrachloride with gaseous chloride ion, i.e.



The required Born-Haber cycle is of the type shown overleaf.

Once $\Delta\text{H}_f^\ominus(\text{K}_2\text{ReX}_6(\text{c}))$, $\Delta\text{H}_f^\ominus(\text{ReX}_4(\text{c}))$ and $\Delta\text{H}_L(\text{K}_2\text{ReX}_6(\text{c}))$ had been determined, use of the cycle illustrated, along with the ancillary thermochemical data (Table 2.11), enabled a value of $\Delta\text{H}_{2\text{X}^-}$ to be estimated for $\text{ReX}_4(\text{c})$. The calculation of $\Delta\text{H}_{2\text{Cl}^-}$ for $\beta\text{-ReCl}_4$ is shown below. From the Born-Haber cycle,

$$\begin{aligned} \Delta\text{H}_f^\ominus(\text{K}_2\text{ReCl}_6(\text{c})) &= 2\Delta\text{H}_f^\ominus(\text{K}^+(\text{g})) + \Delta\text{H}_f^\ominus(\text{ReCl}_4(\text{c})) \\ &\quad + 2\Delta\text{H}_f^\ominus(\text{Cl}^-(\text{g})) + \Delta\text{H}_{2\text{Cl}^-} + \Delta\text{H}_L \end{aligned}$$

$$-1333.1 = 1029.3 - 360.7 - 492.0 - 1502.6 + \Delta\text{H}_{2\text{Cl}^-}$$

$$\Delta\text{H}_{2\text{Cl}^-} = 360.7 + 492.0 + 1502.6 - 1333.1 - 1029.3$$

$$\therefore \underline{\Delta\text{H}_{2\text{Cl}^-} = -7.1 \text{ kJ mol}^{-1}}$$

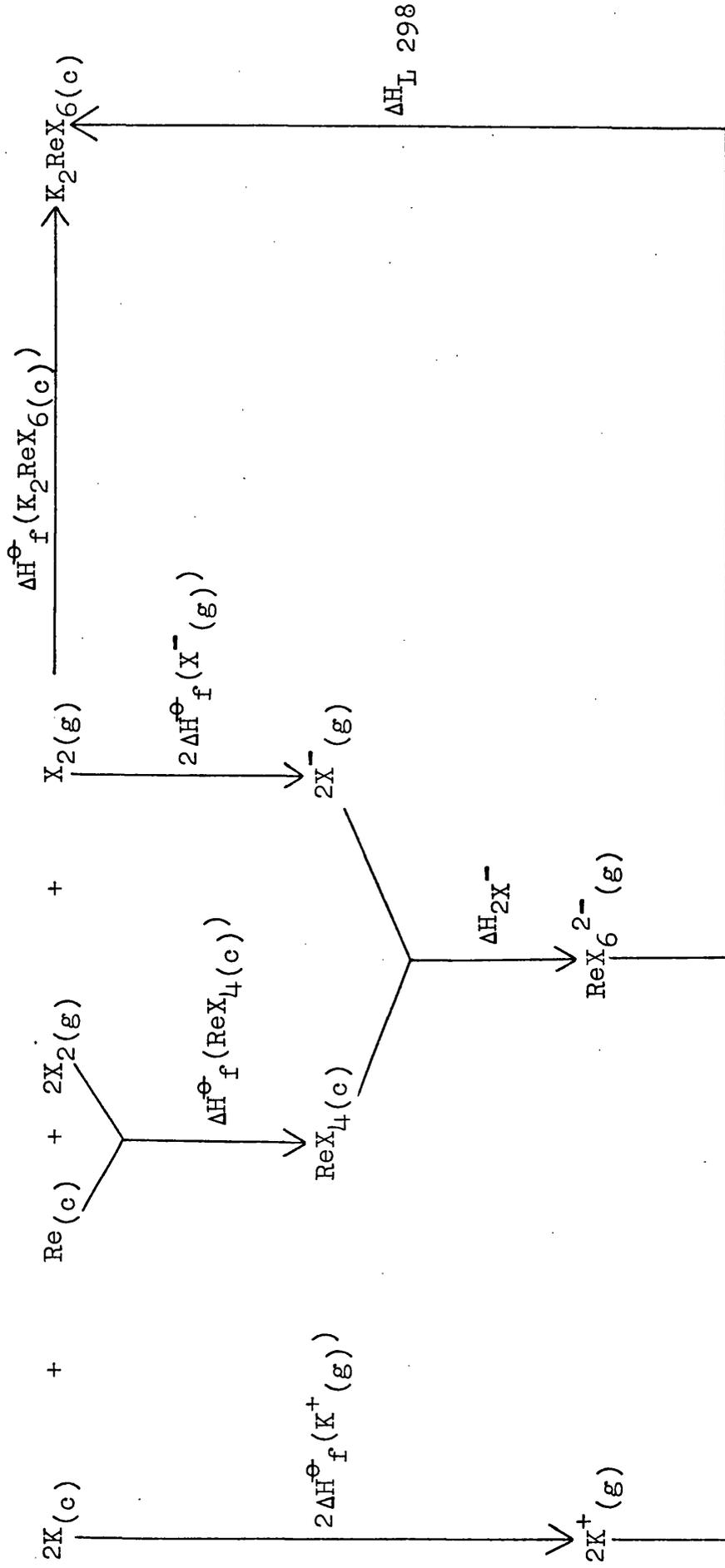
$$\text{Standard deviation} = \underline{\pm 16.1 \text{ kJ mol}^{-1}}$$

Similarly, the sum of the first and second enthalpy changes for the reaction of crystalline rhenium tetrabromide with gaseous bromide ion is given below,

$$\therefore \underline{\Delta\text{H}_{2\text{Br}^-} = +135.4 \text{ kJ mol}^{-1}}$$

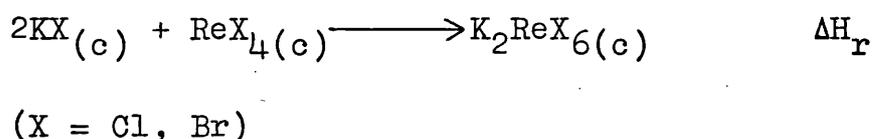
$$\text{Standard deviation} = \underline{\pm 20.0 \text{ kJ mol}^{-1}}$$

BORN-HABER THERMOCHEMICAL CYCLE



In addition, the standard enthalpies of formation of $\text{ReCl}_6^{2-}(\text{g})$ and $\text{ReBr}_6^{2-}(\text{g})$ have been determined as -859.8 and $-620.6 \text{ kJ mol}^{-1}$ respectively.

The differences in Lewis acidity of the two rhenium tetrahalides may be attributable to the ability of chloride ligands to stabilise higher oxidation states more readily than bromide ligands. For the reaction,



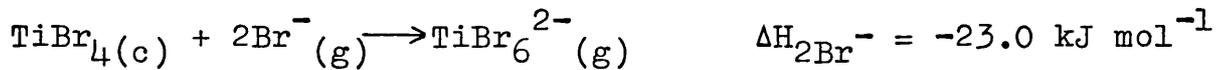
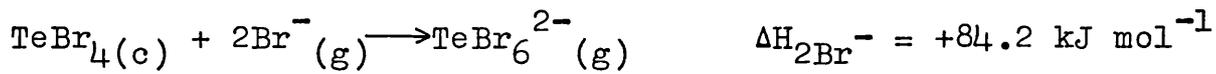
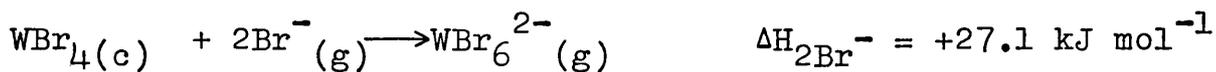
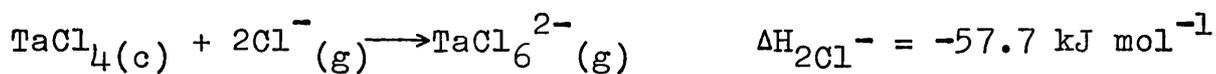
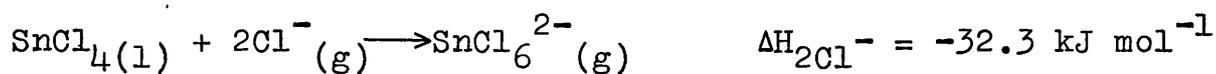
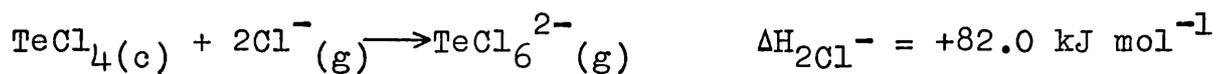
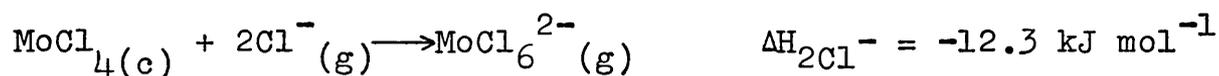
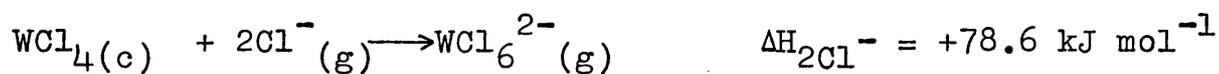
the enthalpy change, ΔH_r , has been calculated to be -102 kJ mol^{-1} for X = Cl and $+51.0 \text{ kJ mol}^{-1}$ for X = Br. (Standard enthalpies of formation of KX are from Reference 29.)

Comparisons with Other Systems

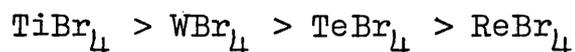
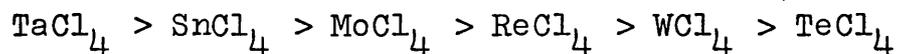
Table 2.12 lists many of the known ΔH_f^\ominus values for hexahalometallate(IV) salts for comparison with potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV). Such a comparison is difficult, but a trend appears to be developing amongst the hexachlorometallates(IV) of the third transition metal series that is analogous to the trend displayed by the divalent chlorides of the first transition metal series.³⁰ There is a noticeably low value at rhenium.

Standard enthalpies of formation for many metal halides are collected together in Table 2.13. Selected thermochemical data from Tables 2.11, 2.12 and 2.13 were

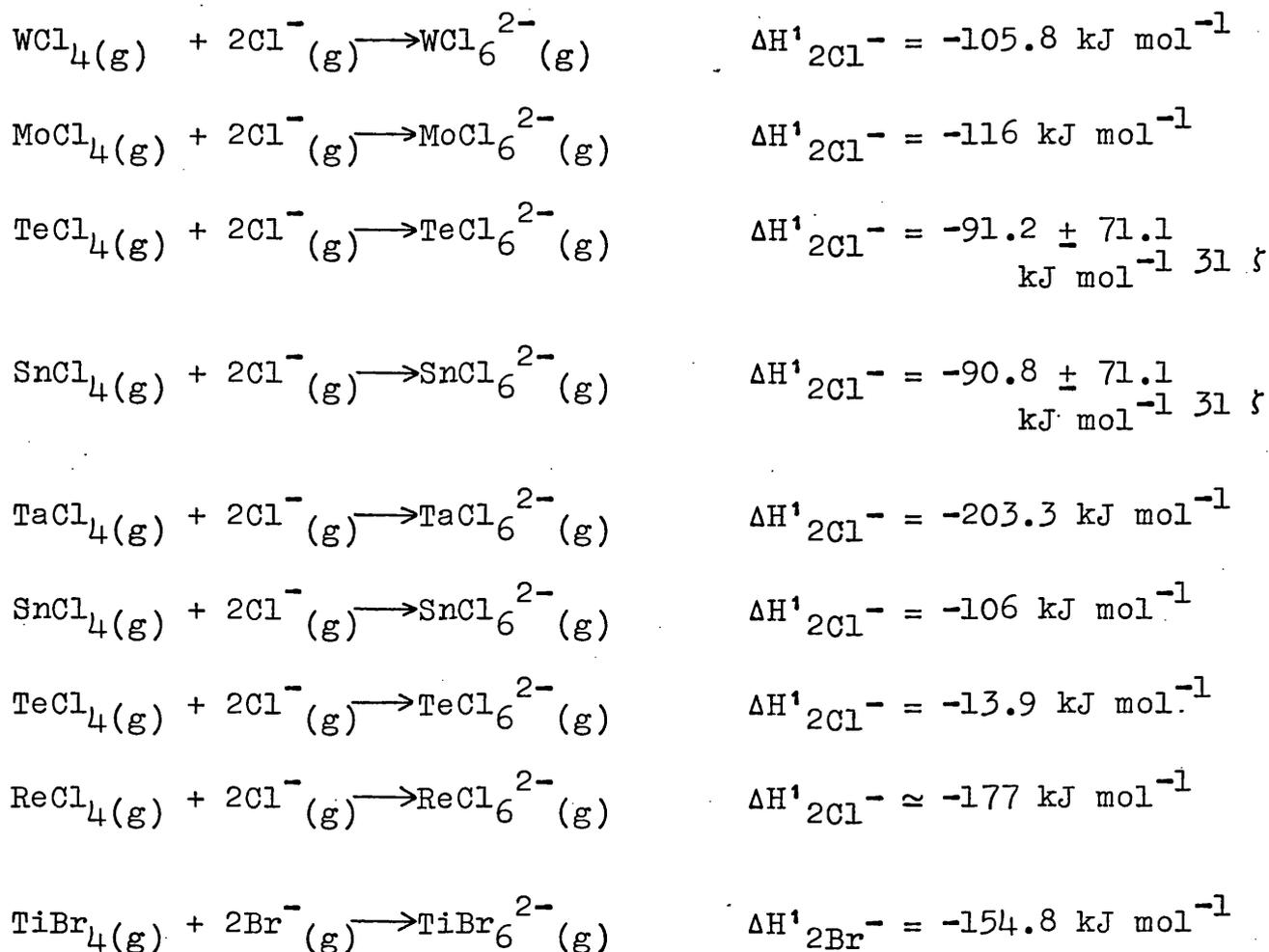
used to estimate the enthalpy changes for the reaction of several tetrahalides with either two gaseous chloride or two gaseous bromide ions. The appropriate reactions and ΔH_{2X^-} values are listed below.



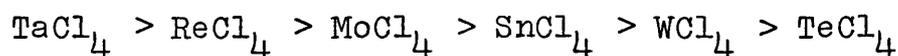
The results suggest that the Lewis acidities of the tetrahalides follow the order:



Although these results are thermochemically more useful, one might expect to observe any inherent trend or pattern by comparing the enthalpies for the reaction of the two gaseous halide ions with the gaseous tetrahalide. By the use of the data in Tables 2.11, 2.12, 2.13 and 2.14, this has been achieved for those tetrahalides whose enthalpies of fusion and vaporisation are known; the results are listed below.



(The approximate value for the gaseous ReCl_4 reaction enthalpy was obtained by assuming an enthalpy of sublimation of ReCl_4 of $\sim 170 \text{ kJ mol}^{-1}$, since the enthalpies of sublimation of TaCl_4 and WCl_4 are 138 and 163 kJ mol^{-1} respectively.) From the above list, the order of Lewis acidities for the gaseous tetrachlorides is:



It may well be that the $\Delta H_{2\text{Cl}^-}$ values above are insufficiently precise to justify such an order. Inherent in these values are systematic and random errors. The systematic errors arise from the approximations involved in the use of the Born-Mayer equation for the calculation of

§ likely limits suggested by the authors

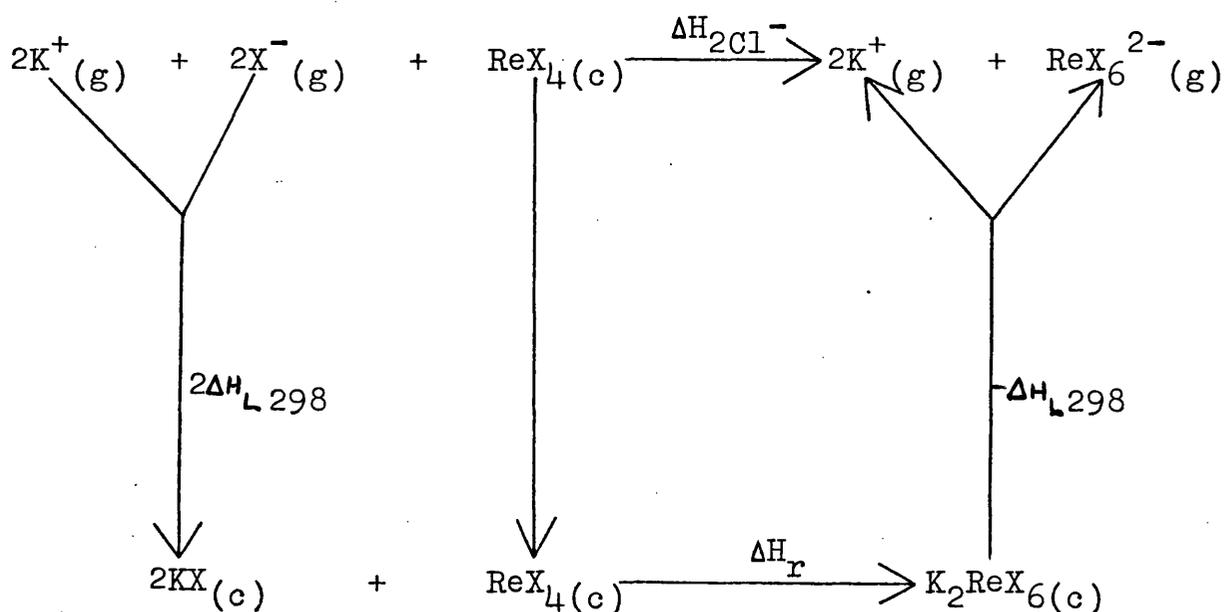
lattice energies. The various models used in the calculation of lattice energies for potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV) in Tables 2.6 and 2.7 give an idea of the range of systematic errors. Webster and Collins³¹ calculated lattice energies for rubidium hexachlorostannate(IV) and hexachlorotellurate(IV), based on various charge distributions on the central metal and on the surrounding chlorides. The authors eventually quoted a large, mainly systematic error (although intuitively) of ± 17 kcal mol⁻¹ (± 71.1 kJ mol⁻¹) for the lattice energies of both salts. These errors were therefore included in the estimation of the enthalpies of the reactions of gaseous tin tetrachloride and of gaseous tellurium tetrachloride with two gaseous chloride ions, viz. -21.7 ± 17 kcal mol⁻¹ (-90.8 ± 71.1 kJ mol⁻¹) and -21.8 ± 17 kcal mol⁻¹ (-91.2 ± 71.1 kJ mol⁻¹) respectively.

Random errors arise from experimental procedure. If the lattice energies obtained from Jolly's procedure for potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV) are substituted for those calculated from the simple Born-Mayer equation, the value of ΔH_{2Cl}^- for β -rhenium tetrachloride becomes -162.7 kJ mol⁻¹ and the value of ΔH_{2Br}^- for rhenium tetrabromide becomes $+8.2$ kJ mol⁻¹. Such a substitution would then alter the order of Lewis acidities postulated earlier, in as much as β -rhenium tetrachloride would then be a stronger chloride ion acceptor in the series. However, if such a charge distribution was calculated for each of the hexachlorometallate(IV) salts by Jolly's method and the lattice energies thence obtained were used to calculate ΔH_{2Cl}^-

values, one might well observe that all the ΔH_{2Cl^-} values were shifted without changing the overall order cited earlier.

The absolute values of ΔH_{2X^-} are of little use because of the large systematic and random errors, particularly if the limits are as large as those for the ΔH_{2Cl^-} values of tin tetrachloride and tellurium tetrachloride quoted by Webster and Collins. However, the differences in the values of ΔH_{2X^-} for various tetrahalides will be much more informative if one uses the same procedure and assumptions in the estimation of those values.

The consistency of the ΔH_{2Cl^-} and ΔH_{2Br^-} determinations above may be assessed by using one further thermochemical cycle. By using these values in the cycle below, the lattice energy of potassium chloride or potassium bromide can be estimated and compared with the values reported in the literature.³²



For KCl:

$$\Delta H_{2Cl^-} = 2\Delta H_L(KCl) + \Delta H_r - \Delta H_L(K_2ReCl_6)$$

$$-7 = 2\Delta H_L(KCl) - 102 + 1510$$

$$\Delta H_L(KCl) = \frac{102 - 7 - 1510}{2}$$

$$\therefore \underline{\Delta H_L(KCl) = -708 \text{ kJ mol}^{-1}}$$

For KBr:

$$\Delta H_{2Br^-} = 2\Delta H_L(KBr) + \Delta H_r - \Delta H_L(K_2ReBr_6)$$

$$135 = 2\Delta H_L(KBr) + 51 + 1437$$

$$\Delta H_L(KBr) = \frac{135 - 51 - 1437}{2}$$

$$\therefore \underline{\Delta H_L(KBr) = -677 \text{ kJ mol}^{-1}}$$

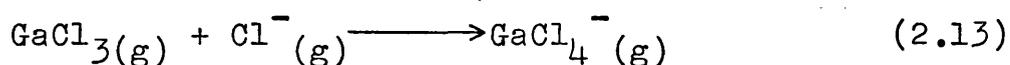
These values are consistent with the reported values of U_L of $-702.9 \text{ kJ mol}^{-1}$ for KCl and $-673.6 \text{ kJ mol}^{-1}$ for KBr. By this method, the values of ΔH_{2X^-} estimated and the assumptions used to calculate these values were shown to be internally consistent

The differences between ΔH_{2Cl^-} and ΔH_{2Br^-} for the tetrahalides of rhenium, tungsten and tellurium are 142.5, 51.5 and 2.2 kJ mol^{-1} respectively. The larger difference estimated between β -rhenium tetrachloride and rhenium tetrabromide reflects the stronger Lewis acid behaviour of the tetrachloride, while the negligible difference between ΔH_{2Cl^-} and ΔH_{2Br^-} for the tellurium tetrahalides is a consequence of their very weak Lewis acid behaviour. Neither of the tungsten tetrahalides appears to be a strong

halide ion acceptor with respect to the rhenium analogues, and tungsten tetrachloride is the weaker Lewis acid of the two. The difference between ΔH_{F^-} and ΔH_{Cl^-} for the two pentahalides of tungsten is $184.9 \text{ kJ mol}^{-1}$,²² attesting to the stronger Lewis acid behaviour of tungsten pentafluoride.

A comparison of the orders of Lewis acidity for the gaseous and crystalline metal tetrahalides above leads to the observation that tin tetrachloride and β -rhenium tetrachloride are the only tetrahalides whose positions alter in the two series. If any significance can be attached to the difference in the order of these two series, it may be that the shuffling of the two tetrachlorides is linked to their unusual structures. Tin tetrachloride is a liquid and β -rhenium tetrachloride is a dimeric crystalline solid, and this will affect the respective enthalpies of sublimation.

The discussion of these derived thermochemical parameters is limited by the paucity of data. However, a comparison of all the above reaction enthalpies with $\Delta H_{Cl^-}^1$ of the Group III acceptor, gallium trichloride,³³ (equation (2.13)) indicates the weakness of the interactions in the above cases.



$$\Delta H_{Cl^-}^1 = -334.7 \pm 12.6 \text{ kJ mol}^{-1}$$

The properties of MX_4 and MX_6^{2-} are both important to the size of ΔH_{2X^-} . Variations on both sides of the equation

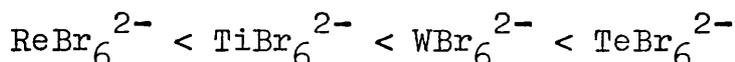
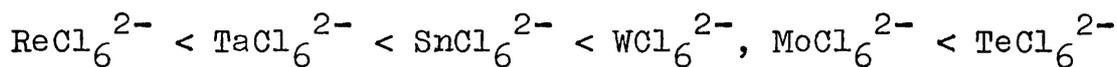
of the reaction can affect any likely trends. To try to explain the above results one needs to examine theoretically such parameters as electronegativities, bond strengths (both σ and π) in MX_4 and MX_6^{2-} , the acceptor strength of M^{4+} , the lattice energy of the gaseous MX_6^{2-} anion, charge distribution, etc. In addition, the differences in d-orbitals in different parts of the Periodic Table might affect the bond strength and type.

Some of these parameters can only be vaguely guessed at, so one must try to examine the system in terms of parameters one can experimentally measure. Experimental parameters one might look at include redox potentials, electron affinities of the M^{4+} and M^+ ions (which are obtained from the fourth and first ionisation potentials of M respectively), radii of MX_4 and MX_6^{2-} , etc.

The only parameter so far examined that appears at all hopeful is the variation in the radius of MX_6^{2-} .³⁴ The values were obtained from the reference by adding together the individual estimated atomic radius of M^{4+} and the estimated atomic diameter of X^- for each MX_6^{2-} anion. The values are:

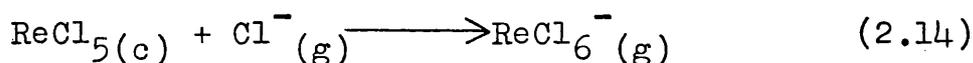
ReCl_6^{2-}	:	4.25 \AA	ReBr_6^{2-}	:	4.53 \AA
WCl_6^{2-}	:	4.36 \AA	WBr_6^{2-}	:	4.64 \AA
MoCl_6^{2-}	:	4.36 \AA	TeBr_6^{2-}	:	4.79 \AA
TeCl_6^{2-}	:	4.51 \AA	TiBr_6^{2-}	:	4.58 \AA
SnCl_6^{2-}	:	4.33 \AA			
TaCl_6^{2-}	:	4.32 \AA			

The anionic radii increase in the following order,



The above order for the hexachlorometallate(IV) anions is similar to that of the Lewis acidities of the gaseous tetrachlorides, although the order is somewhat tentative because of the small differences in anionic radii. Once more, the two dissenters in the otherwise similar arrangement of the two series are the tetrachlorides of tin and rhenium. The reason for the slightly dissimilar orders may well be due partly to the unusual structures of tin tetrachloride and β -rhenium tetrachloride at standard temperature and pressure (which would be reflected in the Lewis acidities via the respective enthalpies of sublimation).

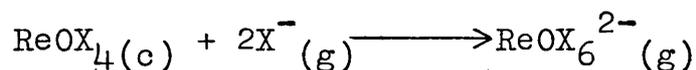
There is still much work to be done on the thermochemistry of rhenium halides. It is impossible, unfortunately, to split the $\Delta H_{2\text{Cl}^-}$ and $\Delta H_{2\text{Br}^-}$ values into the enthalpy changes for the reaction of ReX_4 with X^- and then of ReX_5^- with X^- because salts of the ReCl_5^- and ReBr_5^- anions are unknown. However, it is possible to prepare a salt of ReCl_6^- , $\text{PCl}_4^+\text{ReCl}_6^-$,³⁵ and this could lead to a value for ΔH_{Cl^-} for the reaction shown in equation (2.14).



Of course, to do this, one would need to determine the standard enthalpy of formation of the PCl_4^+ cation and also to estimate the lattice energy of $\text{PCl}_4^+\text{ReCl}_6^-$. This salt

can be made because of the large size of the PCl_4^+ cation, and one could probably make the Ph_4As^+ salt for the same reason. Moreover, it may well prove possible to prepare CsReCl_6 from the reaction of CsCl and ReCl_5 in ICl in a sealed, evacuated Carius tube.

The existence of potassium salts of ReOCl_6^{2-} and possibly ReOBr_6^{2-} has been suggested¹² and, if one could estimate the lattice energies of the salts (using the Kapustinskii equation), the Lewis acidities of the rhenium oxide tetrahalides could be studied, i.e.



One drawback in this case is that the asymmetry of the ReOX_6^{2-} anion would make lattice energy calculations even more difficult than for the A_2MX_6 salts.

CONCLUSION

The enthalpies of alkaline hydrolysis of potassium hexachlororhenate(IV), potassium hexabromorhenate(IV), β -rhenium tetrachloride and rhenium tetrabromide and the oxidative hydrolysis of rhenium oxide tetrachloride have been measured. From these values the respective enthalpies of formation of these compounds have been estimated. Values for the Lewis acidity, $\Delta\text{H}_{2\text{X}}^-$, have thence been estimated as -7.1 kJ mol^{-1} for $\beta\text{-ReCl}_4(\text{c})$ and $+135.4 \text{ kJ mol}^{-1}$ for $\text{ReBr}_4(\text{c})$, where $\Delta\text{H}_{2\text{X}}^-$ is the enthalpy change for the reaction,

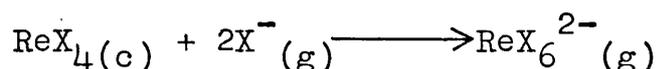


TABLE 2.1 Hydrolysis of potassium hexachlororhenate(IV)
in 2.0 molar sodium hydroxide at 298.2K

Compound	Sample Number	Hydrolysis Number	$\Delta H_{\text{hydrol.}}$ at 298.2K/ kJ mol ⁻¹
K ₂ ReCl ₆	1	1	-264.6
		2	-267.1
		3	-263.6
	2	1	-257.1
		2	-259.2
		3	-261.3
	3	1	-277.4
		2	-261.5
		3	-263.9

Mean enthalpy of hydrolysis = -264.0 kJ mol⁻¹ a

Standard deviation = ±5.4 kJ mol⁻¹

Standard error of the mean = ±1.8 kJ mol⁻¹

90% confidence limits = ±3.4 kJ mol⁻¹

a The computer programme used to calculate mean values, with the attendant standard deviation, standard error of the mean and 90% confidence limits, is detailed in Appendix 3a.

TABLE 2.2 Hydrolysis of potassium hexabromorhenate(IV)
in 2.0 molar sodium hydroxide at 298.2K

Compound	Sample Number	Hydrolysis Number	$\Delta H_{\text{hydrolysis}}$ at 298.2K/ kJ mol ⁻¹
K ₂ ReBr ₆	1	1	-266.5
		2	-286.0
		3	-291.5
		4	-315.9
		5	-282.8
		6	-284.1
	2	1	-300.2
		2	-274.4
		3	-291.6
		4	-286.1
		5	-290.2
	3	1	-288.4
		2	-286.9
		3	-287.7
		4	-285.9
5		-283.5	

Mean enthalpy of hydrolysis = -287.6 kJ mol⁻¹

Standard deviation = ± 10.3 kJ mol⁻¹

Standard error of the mean = ± 2.6 kJ mol⁻¹

90% confidence limits = ± 4.5 kJ mol⁻¹

TABLE 2.3 Hydrolysis of β -rhenium tetrachloride
in 2.0 molar sodium hydroxide at 298.2K

Compound	Sample Number	Hydrolysis Number	$\Delta H_{\text{hydroly.}}$ at 298.2K/ kJ mol ⁻¹
$\beta\text{-ReCl}_4$	1	1	-389.1
		2	-399.6
		3	-412.1
	2	1	-395.4
		2	-421.7
		3	-419.2
	3	1	-380.2
		2	-400.7
		3	-376.9

Mean enthalpy of hydrolysis = $-399.6 \text{ kJ mol}^{-1}$

Standard deviation = $\pm 15.1 \text{ kJ mol}^{-1}$

Standard error of the mean = $\pm 5.0 \text{ kJ mol}^{-1}$

90% confidence limits = $\pm 9.4 \text{ kJ mol}^{-1}$

TABLE 2.4 Hydrolysis of rhenium tetrabromide in
2.0 molar sodium hydroxide at 298.2K

Compound	Sample Number	Hydrolysis Number	$\Delta H_{\text{hydrol.}}$ at 298.2K/ kJ mol ⁻¹
ReBr ₄	1	1	-305.0
		2	-294.1
		3	-293.7
	2	1	-254.4
		2	-257.7
		3	-248.1
		4	-251.0
	3	1	-283.7
		2	-274.5
		3	-285.8
		4	-274.1
		5	-278.2
		6	-275.3

Mean enthalpy of hydrolysis = -274.9 kJ mol⁻¹

Standard deviation = ± 17.2 kJ mol⁻¹

Standard error of the mean = ± 4.8 kJ mol⁻¹

90% confidence limits = ± 8.5 kJ mol⁻¹

TABLE 2.5 Hydrolysis of rhenium oxide tetrachloride
in 2.0 molar hydroxide at 298.2K

Compound	Sample Number	Hydrolysis Number	$\Delta H_{\text{hydrol.}}$ at 298.2K/ kJ mol ⁻¹
ReOCl ₄	1	1	-585.8
		2	-593.7
	2	1	-541.0
		2	-566.1
		3	-562.7
	3	1	-550.2
		2	-577.8
		3	-576.6

Mean enthalpy of hydrolysis = -569.2 kJ mol⁻¹

Standard deviation = ± 16.6 kJ mol⁻¹

Standard error of the mean = ± 5.9 kJ mol⁻¹

90% confidence limits = ± 11.2 kJ mol⁻¹

TABLE 2.6 Variation in lattice energy of K_2ReCl_6
with change in charge distribution

Model	I	II	III	IV	V	VI	VII
Charge on Re	-2	-1.5	-1	-0.5	-0.225	0	+1
$r_o/\text{\AA}$	4.261	4.035	3.832	3.648	3.552	3.481	2.806
Coulombic Energy/ kJ mol^{-1}	-1643.0	-1125.7	-820.3	-727.1	-766.4	-845.6	-1720.2
Repulsion($c \times \frac{0.345}{r_o}$)/ kJ mol^{-1}	133.0	96.2	73.8	68.7	74.4	83.8	211.5
Total $U_I/\text{kJ mol}^{-1}$	-1510.0	-1029.5	-746.5	-658.4	-692	-761.8	-1508.7
Correction for lattice energy of $ReCl_6^{2-}$ (g)/ kJ mol^{-1}	0	410.4	748.0	705.1	662.2	585.8	183.7
Nett $U_I/\text{kJ mol}^{-1}$	-1510.0	-1439.9	-1494.9	-1363.5	-1354.2	-1347.7	-1325.0

TABLE 2.7 Variation in lattice energy of K_2ReBr_6
with change in charge distribution

Model	I	II	III	IV	V	VI	VII
Charge on Re	-2	-1.5	-1	-0.5	-0.344	0	+1
$r_o/\text{\AA}$	4.497	4.258	4.043	3.849	3.792	3.673	2.962
Coulombic Energy/ kJ mol^{-1}	-1556.7	-1066.7	-777.3	-688.9	-702.5	-801.5	-1629.9
Repulsion($c \times \frac{0.345}{r_o}$)/ kJ mol^{-1}	119.4	86.4	66.3	61.8	63.9	75.3	202.4
Total $U_L/\text{kJ mol}^{-1}$	-1437.3	-980.2	-710.9	-627.2	-638.6	-726.0	-1440.1
Correction for lattice energy of $ReBr_6^{2-}$ (g)/ kJ mol^{-1}	0	393.5	619.4	672.6	655.0	556.9	179.5
Nett $U_L/\text{kJ mol}^{-1}$	-1437.3	-1373.7	-1330.3	-1295.6	-1293.7	-1282.9	-1260.6

TABLE 2.8 Ancillary thermochemical data

Species	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	Reference
$\text{ReO}_2 \cdot 2\text{H}_2\text{O}(\text{c})$	-1011.7 ± 6.3	<u>a</u>
$\text{ReO}_4^- (\text{aq})$	-791.6	<u>a</u>
$\text{Cl}^- (\text{aq})$	-167.2	<u>b</u>
$\text{Br}^- (\text{aq})$	-121.5	<u>b</u>
$\text{H}_2\text{O}(\text{l})$	-285.8	<u>b</u>
$\text{OH}^- (\text{aq})$	-230.0	<u>b</u>
$\text{K}^+ (\text{aq})$	-251.2	<u>c</u>
$\text{OCl}^- (\text{aq})$	-109.6	<u>d</u>

a R. H. Busey, K. H. Gayer, R. A. Gilbert and R. B. Bevan Jr., J. Phys. Chem., 1966, 70, 2609.

b National Bureau of Standards, Technical Note 270/3, Washington D.C., 1969.

c National Bureau of Standards, Circular 500, 'Selected Values of Chemical Thermodynamic Properties', Washington D.C., 1952.

d J. E. McDonald, J. P. King and J. W. Cobble, J. Phys. Chem., 1960, 64, 1345.

TABLE 2.9 Mean enthalpies of hydrolysis and standard enthalpies of formation

Compound	Experimental $\overline{\Delta H}_{\text{hydrol.}}^{\text{a}} /$ kJ mol ⁻¹	Calculated $\Delta H_f^{\ominus} /$ kJ mol ⁻¹
K ₂ ReCl ₆	-264.0	-1333.1
K ₂ ReBr ₆	-287.6	-1036.0
β-ReCl ₄	-399.6	- 360.7
ReBr ₄	-274.9	- 303.0
ReOCl ₄	-569.2	- 600.1

a Mean enthalpy of hydrolysis at 298.2K

TABLE 2.10 Crystallographic data and lattice enthalpies for potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV)

Complex Salt	$a_o / \text{\AA}$	$r_o / \text{\AA}$	ΔH_L	Reference
K ₂ ReCl ₆	9.840	4.261	-1503	<u>a</u>
K ₂ ReBr ₆	10.385	4.497	-1445	<u>a</u>

a H. D. Grundy and I. D. Brown, Canad. J. Chem., 1970, 48, 1151.

TABLE 2.11 Ancillary thermochemical data

Species	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	Reference
$\text{K}^+(\text{g})$	-514.6	<u>a</u>
$\text{Cl}^-(\text{g})$	-246.0	<u>b</u>
$\text{Br}^-(\text{g})$	-233.9	<u>b</u>

a D. A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry', Cambridge, 1968.

b National Bureau of Standards, Technical Note 270/3, Washington D.C., 1969.

TABLE 2.12 Standard enthalpies of formation and lattice energies for hexachloro- and hexabromometallate(IV) alkali metal salts

Compound	$\Delta H_f^\ominus /$ kJ mol ⁻¹	U_L 298/ kJ mol ⁻¹	$\Delta H_f^\ominus(\text{MX}_6^{2-}(\text{g}))/$ kJ mol ⁻¹	Reference
K ₂ ReCl ₆	-1333.1	-1510.0	- 859.8	This work
K ₂ ReCl ₆	-1331.0	-1506.2	-	<u>a</u>
K ₂ WCl ₆	-1359.0	-1506.2	- 882.0	<u>b</u>
Rb ₂ WCl ₆	-1429.3	-1489.5	- 922.2	<u>b</u>
Cs ₂ WCl ₆	-1446.0	-1460.2	- 905.4	<u>b</u>
K ₂ MoCl ₆	-1469.4	-1510.4	- 988.3	<u>c</u>
Rb ₂ MoCl ₆	-1494.5	-1493.7	- 983.2	<u>c</u>
Cs ₂ MoCl ₆	-1527.2	-1464.4	- 982.4	<u>c</u>
Na ₂ PtCl ₆	-1142.2	-	-	<u>d</u>
K ₂ TaCl ₆	-1707.1	-1485.3	-1251.0	<u>e,f</u>
Rb ₂ TaCl ₆	-1736.4	-1460.2	-1258.5	<u>e,f</u>
Cs ₂ TaCl ₆	-1774.0	-1435.1	-1258.5	<u>e,f</u>
K ₂ SnCl ₆	-1518.4	-1481.1	-1066.5	<u>d</u>
Rb ₂ SnCl ₆	-1529.3	-1439.3	-1072.4	<u>g</u>
Rb ₂ TeCl ₆	-1231.8	-1481.1	- 733.0	<u>g</u>
K ₂ ReBr ₆	-1036.0	-1437.3	- 620.6	This work
K ₂ WBr ₆	-1065.2	-1460.2	- 634.3	<u>h</u>
Rb ₂ WBr ₆	-1106.2	-1422.6	- 664.4	<u>h</u>
Cs ₂ WBr ₆	-1133.0	-1401.6	- 651.0	<u>h</u>
K ₂ TeBr ₆	- 972.4	-	-	<u>i,j,k</u>
Rb ₂ TeBr ₆	- 984.1	-	-	<u>i,j,k</u>
Cs ₂ TeBr ₆	-1032.2	-1359.8	- 592.0	<u>i,j,k</u>
Rb ₂ TiBr ₆	-1612.1	-1418.4	-1176.1	<u>l</u>
Cs ₂ TiBr ₆	-1641.4	-1393.3	-1167.8	<u>l</u>

contd...

TABLE 2.12 (contd.)

- a R. H. Busey, K. H. Gayer, R. A. Gilbert and R. B. Bevan Jr.,
J. Phys. Chem., 1966, 70, 2609.
- b D. V. Korol'kova and G. M. Kudryashova, Russ. J. Inorg.
Chem., 1970, 15, 1759.
- c A. I. Efimov and L. P. Belorukova, Russ. J. Inorg. Chem.,
1967, 12, 792.
- d National Bureau of Standards, Circular 500, 'Selected
Values of Chemical Thermodynamic Properties', Washington D.C.,
1952.
- e V. M. Tsintsius and E. K. Smirnova, Russ. J. Inorg. Chem.,
1969, 14, 1729.
- f E. K. Smirnova and I. V. Vasil'kova, Russ. J. Inorg. Chem.,
1967, 12, 292.
- g M. Webster and P. H. Collins, J. Chem. Soc. (Dalton Trans.),
1973, 588.
- h P. Taylor, Ph.D. thesis, Leicester, 1975, chapter 5.
- i B. D. Stepin, V. E. Plyushchev, N. M. Selvanova and
G. M. Serebrennikova, Russ. J. Phys. Chem., 1968, 42, 1233.
- j I. D. Brown, Canad. J. Chem., 1964, 42, 2758.
- k A. K. Das and I. D. Brown, Canad. J. Chem., 1966, 44, 939.
- l S. A. Shchukarev, D. V. Korol'kova and I. V. Vasil'kova,
Russ. J. Inorg. Chem. 1964, 9, 980.

TABLE 2.13 Standard enthalpies of formation of binary metal halides and metal oxide halides in the crystalline state

Compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	Reference
<u>Metal halide</u>		
ReCl ₃ (c)	-263.6	<u>a</u>
β -ReCl ₄ (c)	-360.7	This work
ReCl ₅ (c)	-372.4	<u>a</u>
WCl ₄ (c)	-468.6	<u>a</u>
WCl ₅ (c)	-496.2	<u>a</u>
α -WCl ₆ (c)	-602.5	<u>a</u>
MoCl ₃ (c)	-387.0	<u>a</u>
MoCl ₄ (c)	-480.3	<u>a</u>
MoCl ₅ (c)	-527.2	<u>a</u>
TeCl ₄ (c)	-323.0	<u>b</u>
SnCl ₄ (l)	-545.2	<u>b</u>
TaCl ₄ (c)	-706.3	<u>b</u>
ReBr ₃ (c)	-167.4	<u>a</u>
ReBr ₄ (c)	-303.0	This work
WBr ₄ (c)	-209.2	<u>c</u>
WBr ₅ (c)	-316.3	<u>a</u>
WBr ₆ (c)	-348.5	<u>a</u>
MoBr ₄ (c)	-321.3	<u>a</u>
TeBr ₄ (c)	-208.4	<u>b</u>
TiBr ₄ (c)	-681.2	<u>b</u>

contd...

TABLE 2.13 (contd.)

Compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	Reference
<u>Metal oxide tetrachloride</u>		
ReOCl ₄ (c)	-600.1	This work
WOCl ₄ (c)	-701.7	<u>a</u>
MoOCl ₄ (c)	-640.2	<u>a</u>

a National Bureau of Standards, Technical Note 270/4, Washington D.C., 1969.

b National Bureau of Standards, Circular 500, 'Selected Values of Chemical Thermodynamic Properties', Washington D.C., 1952.

c I. L. Quill, 'Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics', McGraw-Hill, London, 1950.

TABLE 2.14 Standard enthalpies of formation
of gaseous metal tetrahalides

Compound	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	Reference
$\text{TeCl}_4(\text{g})$	-227.1	<u>a</u>
$\text{TaCl}_4(\text{g})$	-560.7	<u>b</u>
$\text{MoCl}_4(\text{g})$	-376.6	<u>c</u>
$\text{WCl}_4(\text{g})$	-305.4	<u>c</u>
$\text{SnCl}_4(\text{g})$	-471.5	<u>d</u>
$\text{TiBr}_4(\text{g})$	-549.4	<u>b</u>

a National Bureau of Standards, Circular 500, 'Selected Values of Chemical Thermodynamic Properties', Washington D.C., 1952.

b National Bureau of Standards, Technical Note 270/5, Washington D.C., 1970.

c National Bureau of Standards, Technical Note 270/4, Washington D.C., 1969.

d National Bureau of Standards, Technical Note 270/3, Washington D.C., 1969.

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CHAPTER 3

SOLUBILITY OF
CAESIUM HEXACHLORORHENATE(IV) AND HEXABROMORHENATE(IV)
IN WATER AND IN MIXED AQUEOUS SOLVENTS

CHAPTER 3SOLUBILITY OF
CAESIUM HEXACHLORORHENATE(IV) AND HEXABROMORHENATE(IV)
IN WATER AND IN MIXED AQUEOUS SOLVENTSINTRODUCTION

Single-ion hydration enthalpies have been estimated and reported for a large number of cations, but for a rather smaller number of anions.¹ Values for hydration enthalpies of anions containing transition metals are almost completely restricted to oxo- anions. One exception is the hexachlororhenate(IV) anion, for which a single-ion hydration enthalpy can be derived from published thermochemical data on the enthalpy of solution of potassium hexachlororhenate(IV).² One reason for the paucity of thermochemical data relating to halo- anions of transition metals is that such complexes are often substitution labile. However, the hexachloro- and hexabromorhenate(IV) anions, where the central rhenium is in the normally kinetically inert d^3 configuration, are sufficiently long lived in solution³ for measurements of solubilities to be made, whence enthalpies of solution may be calculated.

The first part of this work deals with the determination of enthalpies of solution of the sparingly soluble caesium salts of the hexachlororhenate(IV) and hexabromorhenate(IV) anions in water. From these enthalpies of solution, single-ion hydration enthalpies of the two anions can be estimated.

The single-ion hydration enthalpy for the hexachloro- anion is in good agreement with the value determined from direct calorimetric measurements of the enthalpy of solution of potassium hexachlororhenate(IV).² The single-ion hydration enthalpy for the hexabromo- anion is the first estimate to be published for this anion.

The second part of this work deals with the solubility of caesium hexachlororhenate(IV) in a range of aqueous-organic binary solvent mixtures. An attempt was made to correlate these solubilities with various empirical solvent parameters, such as Y^4 , Z^5 , E_T^6 and S^7 values, solvent composition⁸ and solvent dielectric constant. Solvent Y values are kinetically based, Z and E_T are spectroscopically based and S values are based on general solvent properties, such as reaction rate, equilibria and spectral shift. Correlation with $g(S)^9$ values was examined because of their basis upon the solubilities of several aromatic compounds in aqueous-organic binary solvent mixtures. Solubilities of caesium hexachlororhenate(IV) were observed to correlate reasonably well with those of sodium hexahydroxoantimonate(V)¹⁰ in the solvent mixtures used. The possibility of estimating the Gibbs free energy of transfer, $\delta_m \mu^\ominus$,¹¹ for the hexachlororhenate(IV) anion, upon change of medium from water to various aqueous-organic mixtures, was also examined.

EXPERIMENTAL

Caesium hexachlororhenate(IV) and hexabromorhenate(IV) were prepared by reducing solutions of ammonium or potassium

perrhenate [tetraoxorhenate(VII)] with iodide ions and then precipitating with caesium chloride or bromide respectively.¹² Saturated solutions of these salts were prepared by equilibrating an excess of solid with the appropriate solvent in a well stirred, thermostatted, reaction vessel. Equilibration times for the hexabromo- complex had to be less than ca. one hour, so that aquation of this complex was negligible. Anion concentrations in the saturated solutions were determined spectrophotometrically. For the hexachloro-anion, the optical density at the frequency of maximum absorption at 35340 cm^{-1} ($\epsilon = 13100\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$)[§] was monitored; for the hexabromo- anion, the maximum absorption frequency is at 28330 cm^{-1} ($\epsilon = 9900\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$).

RESULTS AND DISCUSSION

Solubility in Water

The least soluble alkali metal salts of the hexachlororhenate(IV) and hexabromorhenate(IV) anions are those of caesium. They are both sufficiently sparingly soluble in water for the estimation of their respective enthalpies of solution, from the temperature variation of solubility products, to be reasonable. However, they are therefore too sparingly soluble for direct calorimetric determination of their enthalpies of solution. In contrast, potassium hexachlororhenate(IV) is sufficiently soluble in water for

§ cf. $\epsilon = 12750\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ at 35500 cm^{-1} (V. W. Meloche and R. L. Martin, *Analyt. Chem.*, 1956, 28, 1671).

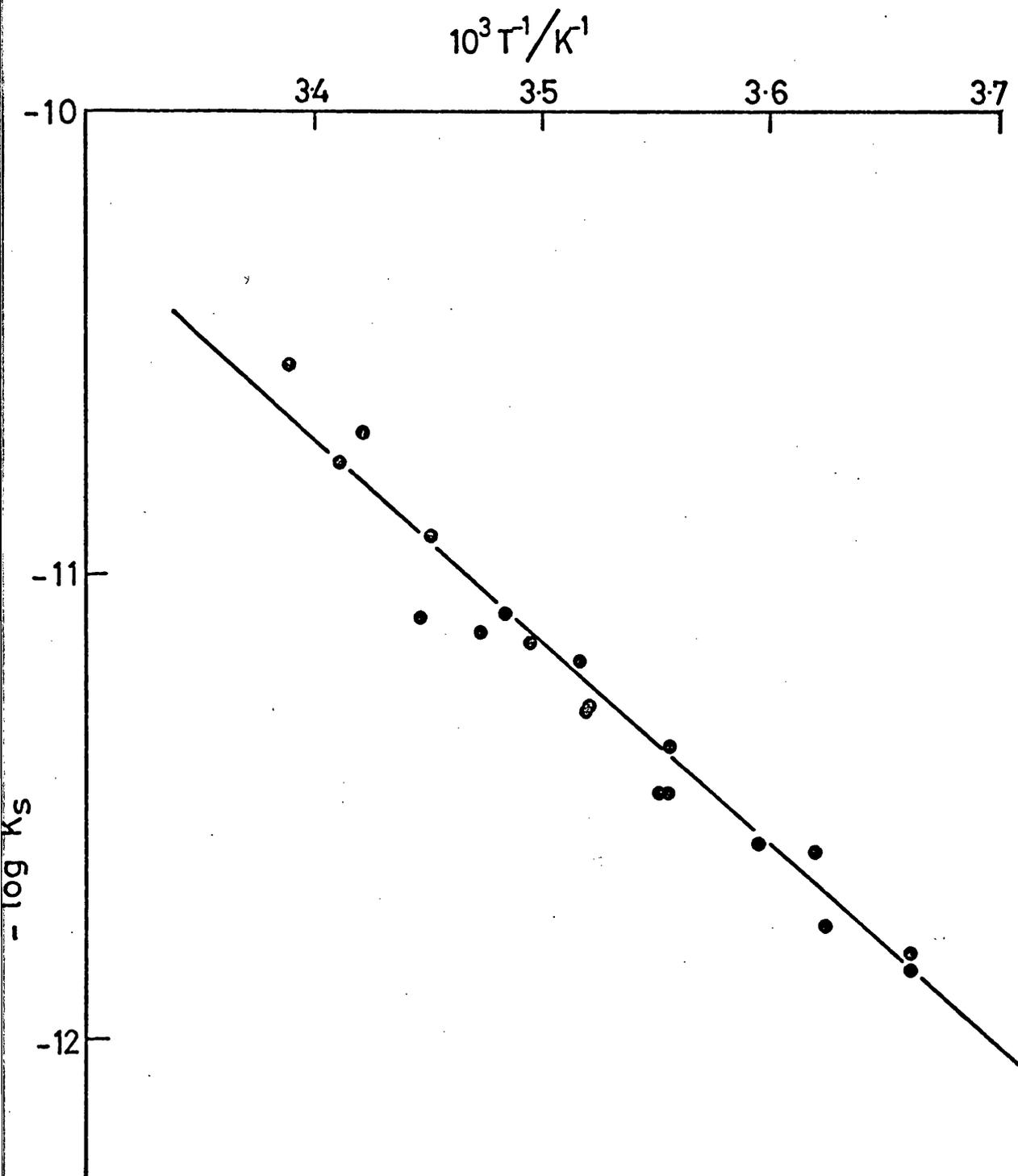
its enthalpy of solution to be determined accurately by calorimetry. It is thus too soluble for the determination of its enthalpy of solution, from the temperature variation of its solubility, to be at all satisfactory without the complementary determination of activity coefficients.¹³

The measured anion concentrations and the solubility products derived for caesium hexachlororhenate(IV) and hexabromorhenate(IV) in aqueous solution over a range of temperatures are reported in Table 3.1. As expected from the Van't Hoff isochore,

$$\text{Log } K_s = - \frac{\Delta H}{2.303RT} + \text{constant},$$

plots of logarithms of these solubility products against reciprocal temperatures are straight lines (Figure 3.1). Least-mean-squares computations of the two sets of results, in Table 3.1, gave enthalpies of solution of $+87.8 \pm 3.6$ and $+95.5 \pm 8.4$ kJ mol⁻¹ for the hexachloro- and hexabromo-complex respectively, assuming that the activity coefficients do not vary with temperature. (These error limits represent the estimated standard errors of the cited means.) The mean ionic activity coefficient at 298.2K can be estimated¹⁴ as 0.97 for each salt; the variation of this with temperature seems unlikely¹⁵ to make a difference of more than 1 kJ mol⁻¹ to the enthalpies of solution cited above. Short extrapolations from the results in Table 3.1 gave values for the solubility products of caesium hexachlororhenate(IV) and hexabromorhenate(IV) in water at 298.2K of 3.4×10^{-11} and 3.2×10^{-12} mol³ dm⁻⁹. From these numbers and the assumed mean ionic activity coefficients of 0.97, the standard Gibbs free energy changes, ΔG^\ominus , of the

FIGURE 3.1 Plot of $\log K_s$ against $\frac{1}{T}$ for Cs_2ReCl_6



solids to the hypothetical solution standard of $m = 1 \text{ mol kg}^{-1}$, may be determined, as shown below for Cs_2ReCl_6 .

Substitution of the solubility product of caesium hexachlororhenate(IV) at 298.2K into the Van't Hoff isotherm on the molar scale,

$$\Delta G^\ominus = -RT \ln K_s,$$

gave ΔG^\ominus of $+60 \text{ kJ mol}^{-1}$. Similarly, ΔG^\ominus for caesium hexabromorhenate(IV) was calculated to be $+66 \text{ kJ mol}^{-1}$.

Thence, from the second law of thermodynamics,

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus,$$

the respective temperature-entropy products, $T\Delta S^\ominus$, are $+28$ and $+30 \text{ kJ mol}^{-1}$ for the hexachloro- and hexabromo- complexes respectively.

To derive single-ion hydration enthalpies from these estimated enthalpies of solution, it is necessary to calculate the lattice energies and thence enthalpies of the salts, and then to separate sums of pairs of ionic-hydration enthalpies into single-ion values. Both these steps require the making of assumptions, as detailed in the following paragraphs.

Caesium hexachlororhenate(IV) and hexabromorhenate(IV) both crystallise with the K_2PtCl_6 (antifluorite) structure, with four molecules per unit cell. The unit cell parameters are $a_0 = 10.260$ and 10.685 \AA respectively¹⁶ (Figure 3.2). From this information, the lattice energies of these two salts can be calculated in a variety of ways. Methods of calculating lattice energies for compounds of the type A_2MX_6 are discussed in Chapter 2, pages 29 - 31, with the consequences of the use of various assumptions described in more detail.

FIGURE 3.2(a) K_2PtCl_6 antiferroite structure

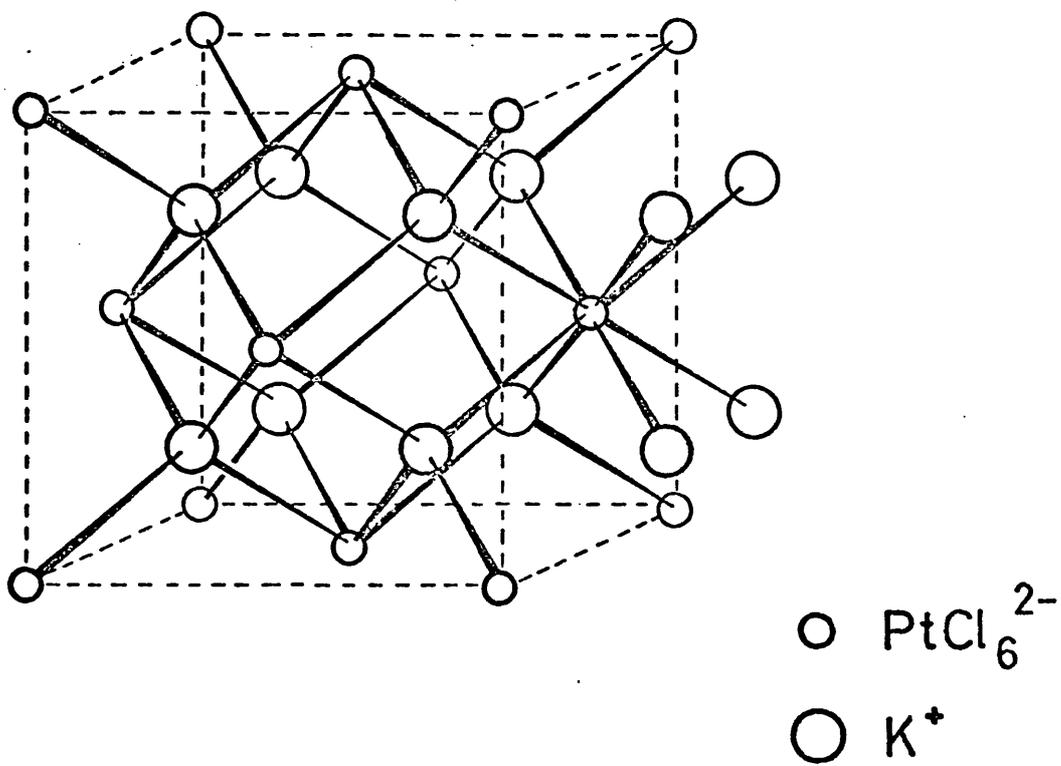
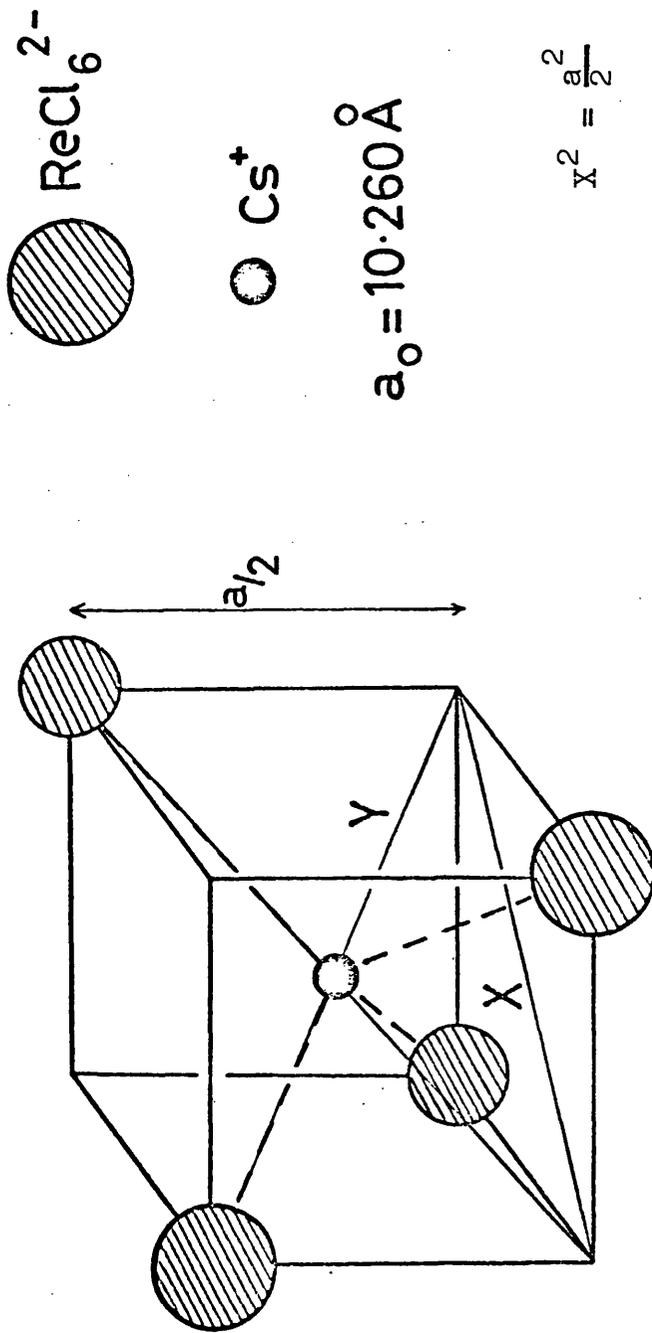


FIGURE 3.2(b) Unit cell of antiferluorite lattice

In one unit cell there is a central caesium cation and four hexachlororhenate(IV) anions disposed tetrahedrally around it.



$$x^2 = \frac{a^2}{2}$$

$$y^2 = \frac{a^2}{2} + \frac{a^2}{4} = \frac{3a^2}{4}$$

$$y = \sqrt{\frac{3a^2}{4}} = 8.8858 \text{ \AA}$$

Thus, Cs-Re distance, $r_0 = \frac{y}{2} = 4.443 \text{ \AA}$

The difficulties associated with lattice energies are well known. For complex salts of known crystal structure, direct lattice sums can be made but, even here, the most serious sources of uncertainty are the charge distribution within the complex ion and the lack of reasonably accurate dispersion energies. The discussion on lattice energies in Chapter 2 illustrates how lattice energy values may be estimated by a lattice-sum calculation, for various assumed charges within the complex anion and for various repulsion terms.

It is possible to calculate charge distributions from quantum mechanical considerations, n.q.r. spectra, X-ray diffraction and electronegativity data. Professor R. D. Peacock has performed lattice-sum calculations, with the use of a suitable computer programme, for various charge distributions within the complex anions of the salts, potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV) (Tables 2.6 and 2.7 respectively). The lattice energy estimates, based on the charge distributions derived from Jolly's electronegativity equalisation procedure (model V in each Table), are of particular interest, if one believes in the electronegativities used. The numbers obtained for simple molecules have been checked against photo-ionisation spectroscopy data and are satisfactory.

The Born-Mayer equation, of course, assumes the formal charge to be distributed evenly over the surface of the complex anion. (Dispersion energy terms are neglected in this equation, which can cause errors of 16 kJ or less in the value of U_L .)

For both pieces of work, the Born-Mayer equation,¹⁷ where one assumes the ions to be completely spherical, was used.

$$U_L = - \frac{N_0 A |z_1| |z_2| e^2}{r_0} \left(1 - \frac{\rho}{r_0}\right)$$

N_0 is the Avogadro number, $6.023 \times 10^{23} \text{ mol}^{-1}$.

A is the Madelung constant;¹⁸ 5.03879 for a regular anti-fluorite lattice.

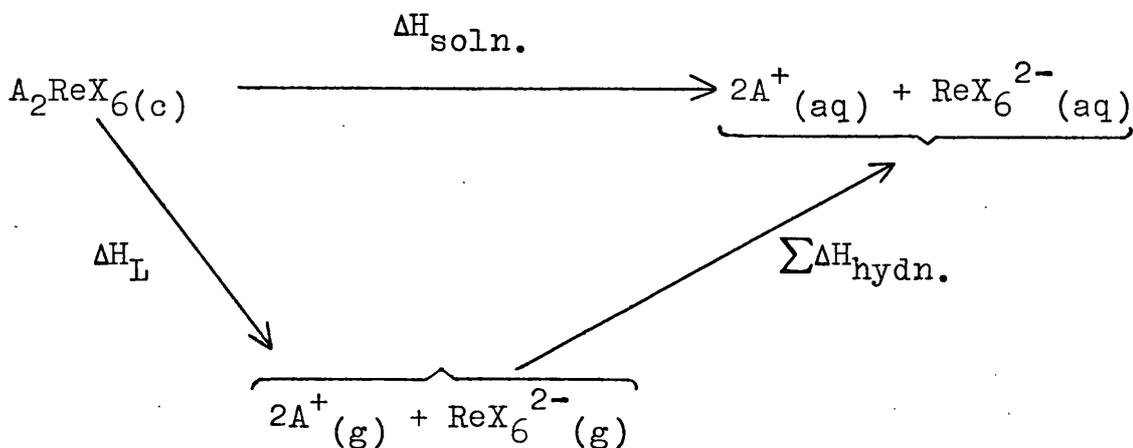
z_1 and z_2 are the charges of the constituent ions.

e is the charge on an electron, $1.60210 \times 10^{-19} \text{ C}$.

r_0 is the distance between cation and anion, measured in \AA .

ρ is the repulsion term, 0.345\AA .

Thence, the estimated lattice energies are -1453 and $-1399 \text{ kJ mol}^{-1}$ respectively, and the lattice enthalpies at 298.2K are -1460 and $-1406 \text{ kJ mol}^{-1}$. Use of a simple thermochemical cycle provides estimates of the sums of the enthalpies of hydration of the gaseous constituent ions.



$$\underline{\underline{\sum \Delta H_{\text{hyd.}} = \Delta H_{\text{soln.}} + \Delta H_L}}$$

From these calculated lattice enthalpies and measured enthalpies of solution, the sums of the enthalpies of hydration of the gaseous constituent ions are $-1372 \text{ kJ mol}^{-1}$ for caesium hexachlororhenate(IV) and $-1312 \text{ kJ mol}^{-1}$ for caesium hexabromorhenate(IV). These sums of ionic hydration enthalpies cannot be separated into their individual ionic constituents without making an assumption.

The field of hydration enthalpy of the proton has been fully reviewed by D. R. Rosseinsky.¹⁹ From this review, the author concludes that the approach used by Halliwell and Nyburg²⁰ is to be preferred, since it makes least use of assumptions and is based on the significance of differences between thermodynamic hydration functions for ions of opposite charge. The big advantage of this method is that errors due to kinetic assumptions are very small; this is not necessarily true of other methods which attempt to determine absolute hydration enthalpies.

The important equation derived from the Halliwell and Nyburg treatment is,

$$\frac{1}{2}\Delta[\Delta H^{\ominus}_{\text{conv.hydn.}}] = \frac{1}{2} \sum_{i=3}^j \frac{c_i}{(R + a)^i} - \Delta H^{\ominus}_{\text{abs.hydn.}} \text{H}^+(\text{g})$$

$\Delta H^{\ominus}_{\text{conv.hydn.}}$ is the conventional enthalpy of hydration (for which the enthalpy of hydration of the proton is zero) referred to the gas phase hydrogen ion; for standard states, 1 molar in solution and 1 atmosphere gas.

$\Delta H^{\ominus}_{\text{abs.hydn.}}$ is the absolute enthalpy of hydration for conventional standard states.

R is the effective radius of the ion.

a is the effective radius of the water molecule.

c_i is the unspecified proportionality constants for the three types of potential energy involved between an ion and a solvent molecule, as used by Buckingham,²¹ viz. energies associated with induced moments for each ion, those associated with the dispersion forces and those associated with the repulsion forces.

Evaluation of $\Delta H^{\ominus}_{\text{abs.hydn.}} H^+(g)$ is carried out graphically. If the leading term of the inverse power series has $i = 3$, then a plot of $\Delta[\Delta H^{\ominus}_{\text{conv.hydn.}}]$ against $(R + a)^{-3}$ should be linear at large $(R + a)$ and should cut the ordinate at $-\Delta H^{\ominus}_{\text{abs.hydn.}} H^+(g)$.

Plots of $\Delta H^{\ominus}_{298 \text{ conv.hydn.}}$ (anions) and $\Delta H^{\ominus}_{298 \text{ conv.hydn.}}$ (cations) against $(R + a)^{-3}$ give two curves, one for anions and one for cations. From these two curves, $\Delta[\Delta H^{\ominus}_{\text{conv.hydn.}}]$ is estimated at selected values of $(R + a)^{-3}$. The values of $\Delta[\Delta H^{\ominus}_{\text{conv.hydn.}}]$ halved are plotted against $(R + a)^{-3}$. This curve becomes linear for large $(R + a)$ values, which vindicates the use of Buckingham's model for aqueous solutions of electrolytes and Halliwell and Nyburg's assumptions concerning differences in kinetic contributions to the internal energy. The final value suggested for

$$\Delta H^{\ominus}_{298 \text{ abs.hydn.}} H^+(g) = -1091 \pm 10.5 \text{ kJ mol}^{-1}.$$

The method proposed by Halliwell and Nyburg, using data for singly-charged ions, has been extended to larger, doubly-

charged, complex ions.²² The result, $\Delta H^{\ominus}_{\text{abs.hydn. H}^+(\text{g})} = -1095 \pm 20 \text{ kJ mol}^{-1}$, is in agreement with, and further confirms, Halliwell and Nyburg's earlier estimate. The Halliwell and Nyburg estimate was chosen for use in this work, since it has a lower standard error.

Upon subtracting $-1091z \text{ kJ mol}^{-1}$ (b) from the conventional values of hydration enthalpy (based on an arbitrary standard of zero for the proton), where z is the charge of the ion, single-ion hydration enthalpies are obtained. Thence, the single-ion hydration enthalpy for the caesium cation is -263 kJ mol^{-1} , and those for the hexachlororhenate(IV) and hexabromorhenate(IV) anions are -846 and -784 kJ mol^{-1} respectively. This value of -846 kJ mol^{-1} for the chloro-anion compares favourably with that of -827 kJ mol^{-1} derived from direct calorimetric determination² of the enthalpy of solution of potassium hexachlororhenate(IV).

It is impossible to put statistically meaningful uncertainty limits to the preceding single-ion hydration enthalpies for the hexachlororhenate(IV) and hexabromorhenate(IV) anions. The uncertainties in these values, which derive from the experimental determination of enthalpies of solution, are less than $\pm 10 \text{ kJ mol}^{-1}$ (see above). The uncertainties derived from the absolute value used for the single-ion hydration enthalpy for the proton are ca. $\pm 10 \text{ kJ mol}^{-1}$.¹⁷ In the present state of knowledge concerning the calculation of lattice energies for salts of this type, it is impossible to assess the uncertainties from this source (ref. Chapter 2, page 29). However, comparisons

between these results and those for other anions, especially of similar type (cf. following paragraph), will be valid provided that the lattice energies are calculated by similar methods.

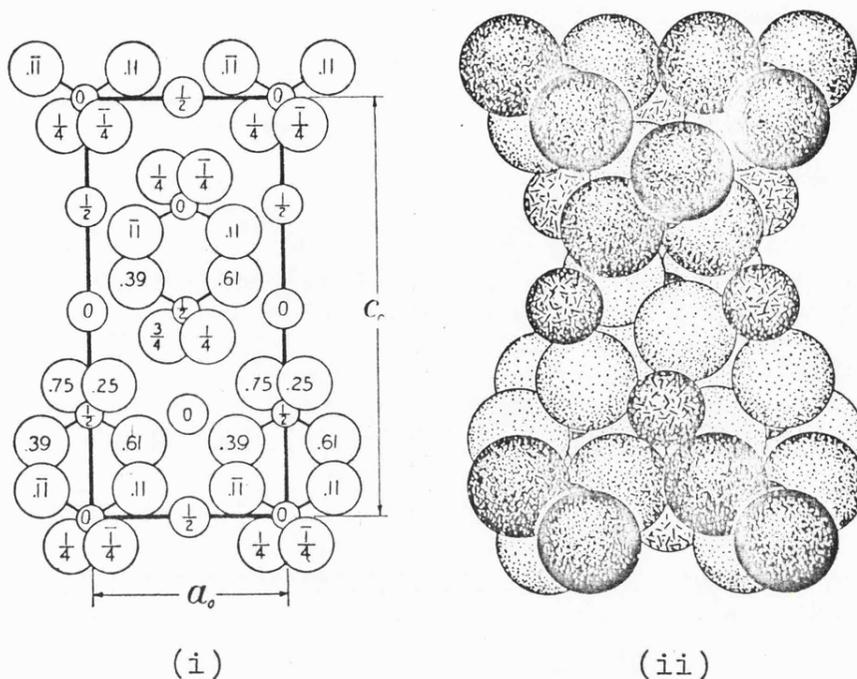
Although few values for single-ion hydration enthalpies of polyatomic anions of the type MX_6^{n-} (X = halogen) are quoted in reviews and textbooks, it is possible to estimate these for several such anions from published solubility data and known crystal structures. This procedure was carried out for some hexachloro- and hexabromometallates, closely related to the hexahalorhenates(IV) which form the subject of this work. The solubility data used in calculating enthalpies of solution are quoted in Table 3.2. The calculations of enthalpies of solution were carried out on the assumption that activity coefficients for these sparingly soluble salts are invariant with temperature. All the salts listed in Table 3.2 crystallise with the K_2PtCl_6 structure; their lattice parameters are listed in Table 3.3. Lattice energies, again calculated using the Born-Mayer equation¹⁷ with $\rho = 0.345\text{\AA}$ and a Madelung constant¹⁸ of 5.03879, are also given in Table 3.3.

From the respective lattice enthalpies and enthalpies of solution, single-ion hydration enthalpies for the various hexahalo- anions were calculated in the manner, and using the assumptions, described above for the hexahalorhenates(IV). The ranges of values for the single-ion hydration enthalpies of the MCl_6^{2-} and MBr_6^{2-} anions, as shown in Table 3.4, are small, since the radius of each hexahalo-anion is dominated by the large chlorides or bromides.

Indeed, the uncertainties in the individual anion values are comparable with the ranges, and it is therefore not possible to confirm the expected trend of anion hydration enthalpies with variation of anion radius.

There do not appear to be any other published single-ion hydration enthalpies for rhenium-containing complex anions with which to compare the results for the two hexahalorhenates(IV). One can estimate a value for the perrhenate anion from the published solubility data and crystal structure of potassium perrhenate. There is disagreement in the literature over the enthalpy of solution of potassium perrhenate in water. An early calorimetric determination (at 21.7 °C) gave +13.8 kcal mol⁻¹ (58 kJ mol⁻¹);²³ subsequent estimates from the temperature variation of solubility gave 7.63²⁴ and 7.68²⁵ kcal mol⁻¹ (31.9 and 32.1 kJ mol⁻¹ respectively). Unfortunately, these authors plotted logarithms of solubilities rather than of solubility products against reciprocal temperatures, and are therefore a factor of two in error. Moreover, these erroneous values, rather than the earlier calorimetric determination, are quoted in a current monograph on rhenium chemistry.²⁶ An enthalpy of solution of potassium perrhenate in water of 64.5 ± 1.3 kJ mol⁻¹ was computed from the values given in ref. 23, and 61.2 ± 1.1 kJ mol⁻¹ from some earlier independent solubility data.²⁷ Both estimates are in tolerable agreement with the calorimetric value which was chosen for this work.

Potassium perrhenate crystallises in the scheelite (CaWO₄) lattice (Figure 3.3), with four molecules in the

FIGURE 3.3 CaWO_4 lattice

- (i) Atoms in the tetragonal unit of CaWO_4 projected on an a face. The oxygen atoms are represented by the large, the tungsten atoms by the smallest circles.
- (ii) A packing drawing of the atoms of CaWO_4 seen along an a_0 axis. Line-shaded spheres are calcium ions, the oxygen atoms are dotted.

unit cell and dimensions of $a = 5.680$ and $c = 12.703\text{\AA}$.²⁸

From the programme detailed in Appendix 3b, the distances of nearest neighbour atoms from each rhenium atom were computed. Each rhenium has four nearest potassium ions at 4.016\AA , and four potassiums and four rheniums at 4.260\AA . Using the value of 4.016\AA for $(r_c + r_a)$ in Kapustinskii's equation²⁹ (derived from the Born-Mayer equation),

$$-U_L = \left[\frac{121.4\nu |z_1| |z_2|}{(r_c + r_a)} \right] \left[1 - \frac{0.0345}{(r_c + r_a)} \right]$$

ν = number of ions in the formula,

a lattice energy of -547 kJ mol^{-1} was calculated. Thence, by the procedures used above, a single-ion hydration enthalpy of -172 kJ mol^{-1} was estimated for the perrhenate anion.³⁰

In accordance with an electrostatic model for ion hydration, this value is somewhat smaller than that for the permanganate ion¹ and much less than those reported above for the hexahalorhenates(IV). In turn, these latter hydration enthalpies are smaller than those for the considerably smaller sulphate anion.¹ The trend of increasing exothermicity of these single-ion hydration enthalpies parallels the decrease in anionic radii, viz. Table 3.5.

Solubility in Mixed Aqueous Solvents

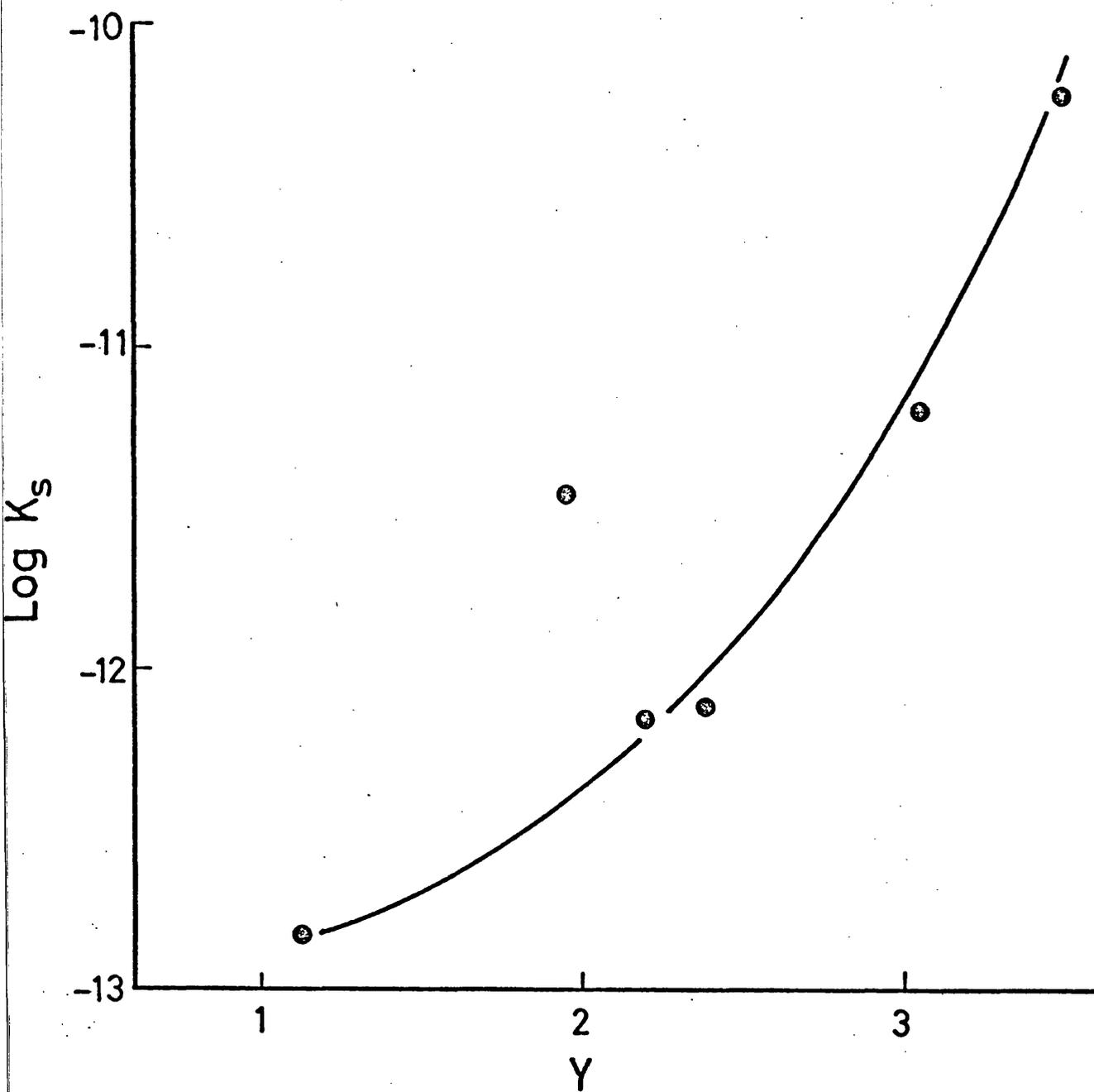
J. Burgess previously tried to correlate the solubility of sodium hexahydroxoantimonate(V) in a range of water-rich mixed aqueous solvents with Grunwald-Winstein solvent Y values.¹⁰ In that case there was a moderately satisfactory correlation ($3.49 \geq Y > \text{ca. } 1$), though the correlation line was curved rather than linear. The solubility of caesium hexachlororhenate(IV) in the same range of mixed aqueous solvents was investigated, as a better and more linear correlation might be expected here. The hexachlororhenate(IV) anion more closely resembles the chloride ion whose solvation determines the reactivities that define solvent Y values. The possibilities of correlating the solubilities of caesium hexachlororhenate(IV) with other solvent parameters, and indeed with the solubilities of sodium hexahydroxoantimonate(V), were also investigated. Further, an attempt was made to

estimate the Gibbs free energy of transfer for ReCl_6^{2-} , $\delta_m \mu^\ominus(\text{ReCl}_6^{2-})$, upon the change of the solvent medium from water to the various mixed aqueous solvents. A comparison was made between $\delta_m \mu^\ominus(\text{ReCl}_6^{2-})$ and $\delta_m \mu^\ominus(\text{Cl}^-)$, since one would expect similar behaviour.

Measured concentrations of the hexachlororhenate(IV) anion and derived (concentration) solubility products are reported, with appropriate values for the various solvent parameters, in Table 3.6. The plot of logarithms of solubility products against solvent Y values was curved, but the points fell tolerably close to a common curve (Figure 3.4). Plots of logarithms of solubility products against other solvent parameters gave poorer correlations, whose relative curvature and scatter could be roughly judged from the computed standard errors of least-mean-squares straight lines. These standard errors were 33% for the attempted correlations with E_T , 36% for the dielectric-constant function $(D - 1)/(2D + 1)$, 37% for $g(S)$, 37% for mole fraction, 42% for S and 47% for D .

A plot of logarithms of solubility products for caesium hexachlororhenate(IV) against those of sodium hexahydroxoantimonate(V) gave better results (Figure 3.5), the standard error of 13% arising mainly from the slight curvature of the correlation line. The gradient of this latter plot was 1.5 ± 0.2 ; the solubility of caesium hexachlororhenate(IV) is more sensitive to solvent variation than that of sodium hexahydroxoantimonate(V). This difference may presumably be attributed primarily to the doubly-negative charge on the hexachlororhenate(IV) anion [estimated anion radii are

FIGURE 3.4 Plot of $\text{Log } K_s$ against solvent Y values for Cs_2ReCl_6 in mixed aqueous solvents



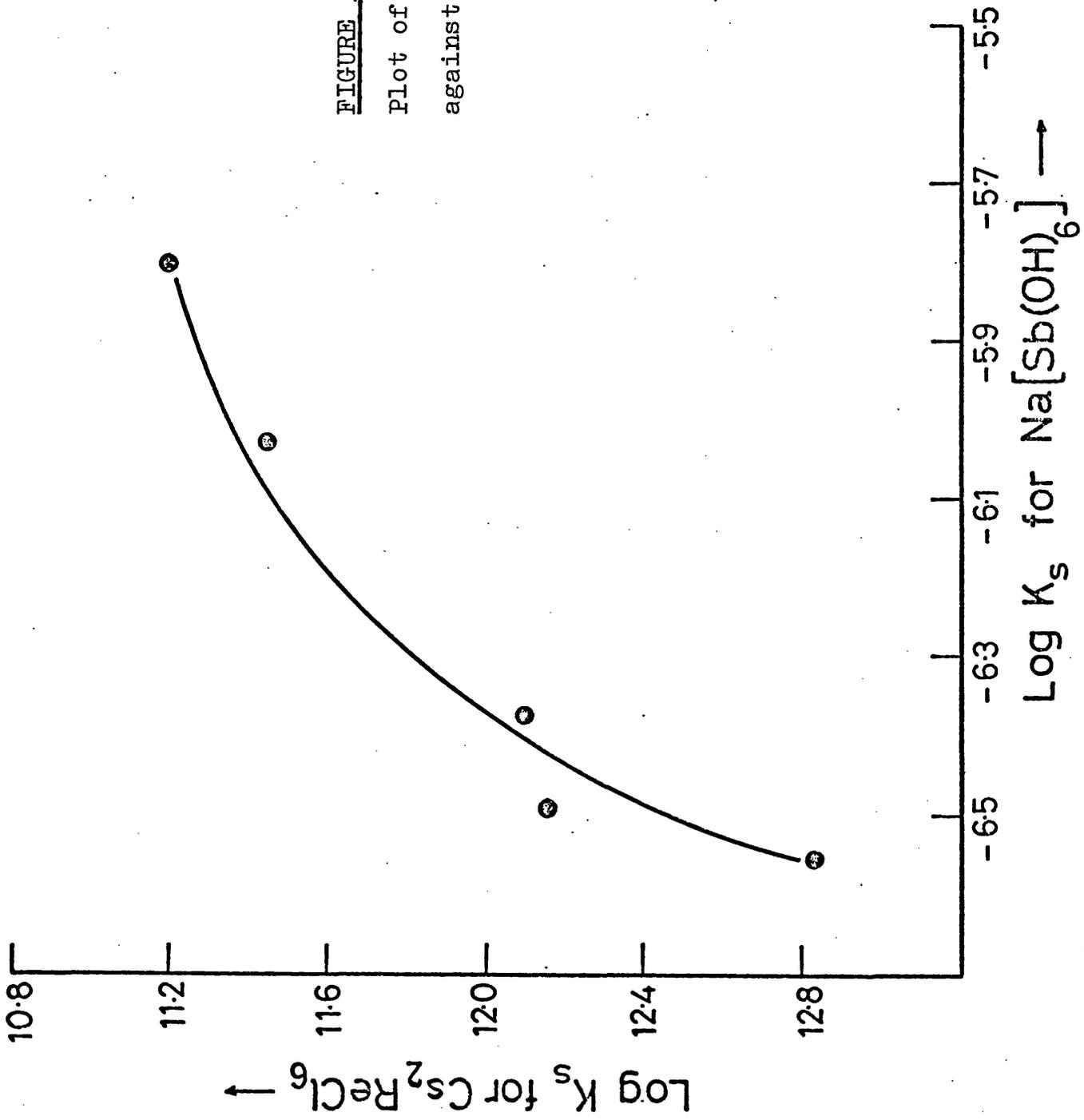


FIGURE 3.5

Plot of Log K_s for Cs₂ReCl₆
against Log K_s for NaSb(OH)₆

4.25Å for ReCl_6^{2-} , 3.7Å for $\text{Sb}(\text{OH})_6^-$; cation radii are 1.69Å for Cs^+ , 0.95Å for Na^+ (ref. 29)].

A value of Gibbs free energy of transfer, on the mole fraction scale, from water to 40% aqueous methanol (by volume) was estimated for caesium hexachlororhenate(IV) by use of the following relationship;

$$\delta_m \mu^\ominus(\text{Cs}_2\text{ReCl}_6) = \mu_2^\ominus(\text{II}) - \mu_2^\ominus(\text{I})$$

on transfer of solute from medium I to medium II (in this case I is water, II is 40% aqueous methanol). Thus,

$$\begin{aligned} \delta_m \mu^\ominus &= -RT \ln K_s(\text{II}) + RT \ln K_s(\text{I}) \\ &= -RT [\ln K_s(\text{II}) - \ln K_s(\text{I})] \\ &= -RT \ln [K_s(\text{II})/K_s(\text{I})] \end{aligned}$$

The estimate obtained was 9.4 kJ mol^{-1} . This value was split into $\delta_m \mu^\ominus(\text{Cs}^+)$ and $\delta_m \mu^\ominus(\text{ReCl}_6^{2-})$ by use of two approximate literature values for $\delta_m \mu^\ominus(\text{Cs}^+)$ ³¹ and the following relationship,

$$\delta_m \mu^\ominus(\text{Cs}_2\text{ReCl}_6) = 2\delta_m \mu^\ominus(\text{Cs}^+) + \delta_m \mu^\ominus(\text{ReCl}_6^{2-})$$

Thence, estimates of $\delta_m \mu^\ominus(\text{ReCl}_6^{2-})$ are $9.4 \pm 0.3 \text{ kJ mol}^{-1}$ and $10.4 \pm 0.2 \text{ kJ mol}^{-1}$ [cf. $\delta_m \mu^\ominus(\text{Cl}^-) = 6.24 \pm 1.0 \text{ kJ mol}^{-1}$]³¹. No $\delta_m \mu^\ominus(\text{Cs}^+)$ values are available for the transfer from water to 40% aqueous ethanol and those for transfer to 40% aqueous dioxane are far from firmly established.

The transfers of both hexachlororhenate(IV) and chloride anions from water to 40% aqueous methanol are unfavourable, and are reflected in the positive values of $\delta_m \mu^\ominus$. Transfer

of the hexachlororhenate(IV) anion is more unfavourable (larger positive $\delta_m \mu^\ominus$) than the chloride anion; this is presumably due to the double negative charge on the hexachlororhenate(IV) anion. This result is in agreement with the larger negative single-ion hydration enthalpy of the hexachlororhenate(IV) anion compared to that of the chloride anion, -837 and $-351^{1(a)}$ kJ mol^{-1} respectively.

CONCLUSION

The enthalpies of solution of caesium hexachlororhenate(IV) and caesium hexabromorhenate(IV) in water have been determined, from the temperature variation of their solubilities, as $+88$ and $+96$ kJ mol^{-1} respectively. Hence, the single-ion enthalpies of hydration of the gaseous hexachlororhenate(IV) and hexabromorhenate(IV) anions have been estimated as -846 and -784 kJ mol^{-1} respectively, based on the Born-Mayer equation to calculate the lattice energies of the two caesium salts and on the assumption that the single-ion hydration enthalpy of the proton is -1091 kJ mol^{-1} . These values fall within the range expected, upon comparison with single-ion hydration enthalpies of other polyatomic anions. Attempts to correlate the solubility of caesium hexachlororhenate(IV) in mixed aqueous solvents with various empirical solvent parameters are described.

From solubility measurements of caesium hexachlororhenate(IV), two estimates of the Gibbs free energy of transfer of the hexachlororhenate(IV) anion, $\delta_m \mu^\ominus(\text{ReCl}_6^{2-})$,

have been determined as 9.4 and 10.4 kJ mol⁻¹, using two different literature estimates for $\delta_m \mu^\ominus(\text{Cs}^+)$, upon transfer from water to 40% vol.% methanol-water.

TABLE 3.1 Measured anion concentrations and calculated (concentration) solubility products (K_s) for saturated aqueous solutions of caesium hexachlororhenate(IV) and hexabromorhenate(IV)

Cs_2ReCl_6		
Temp./K	$10^5[\text{ReCl}_6^{2-}]/\text{mol dm}^{-3}$	$10^{13}K_s/\text{mol}^3 \text{ dm}^{-9}$
273.2	7.10	14.3
273.2	7.25	15.3
276.0	7.60	17.5
276.3	8.55	25.0
278.2	8.70	26.4
281.2	10.23	42.8
281.3	9.47	33.9
281.7	9.47	33.9
284.0	10.92	52.0
284.2	10.84	50.9
284.3	11.76	65.0
286.1	12.14	71.5
287.0	12.75	82.9
287.9	12.37	75.6
289.8	14.50	122.0
290.2	12.67	81.4
292.3	17.18	202.7
293.2	16.41	176.8
295.1	19.24	284.7

contd...

TABLE 3.1 (contd.)

Cs ₂ ReBr ₆		
Temp./K	$10^5[\text{ReBr}_6^{2-}]/\text{mol dm}^{-3}$	$10^{13}K_s/\text{mol}^3 \text{ dm}^{-9}$
273.2	3.28	1.4
274.2	3.38	1.6
275.2	3.23	1.4
277.8	3.03	1.1
280.0	4.14	2.8
280.4	4.55	3.8
282.6	3.64	1.9
284.6	4.55	3.8
285.2	4.95	4.8
286.5	5.56	6.9
288.8	5.66	7.2
290.9	7.47	16.7
292.4	7.58	17.4
293.5	7.83	19.2
295.4	8.89	28.1

TABLE 3.2 Computed enthalpies of solution ($\Delta H_{\text{soln.}}$)
of salts A_2MX_6 in water

Salt	Ref.	Temp. range/K	n^a	$\Delta H_{\text{soln.}}^b /$ kJ mol ⁻¹	SEM ^c / kJ mol ⁻¹
Cs ₂ ReCl ₆	<u>d</u>	273.2 - 295.1	19	+88	4
Cs ₂ ReBr ₆	<u>d</u>	273.2 - 300.7	15	+96	8
Cs ₂ PtCl ₆	<u>e</u>	273.2 and 373.2	2	+70	
K ₂ PtCl ₆	<u>f</u>			+56	
K ₂ PtBr ₆	<u>f</u>			+51	
K ₂ SnCl ₆	<u>g</u>			+50	
(NH ₄) ₂ PtCl ₆	<u>h</u>	273.3 - 372.2	12	+62	1
(NH ₄) ₂ PtBr ₆	<u>h</u>	273.4 - 372.2	12	+54	2
(NH ₄) ₂ IrCl ₆	<u>h,i</u>			+61 ^j	

a Number of solubility determinations.

b Assuming that activity coefficients do not vary with temperature.

c Standard error of the mean.

d This work.

e 'Handbook of Chemistry and Physics', 53rd edition, ed. R. C. Weast, Chemical Rubber Co., Cleveland, Ohio, 1973, pp. B63 et seq.

f 'Handbook of Chemistry', tenth edition, ed. N. A. Lange, McGraw-Hill, New York, 1967.

g 'Selected Values of Chemical Thermodynamic Properties', National Bureau of Standards Circular 500, 1952.

h E. H. Archibald and J. W. Kern, Trans. Roy. Soc. Canad., 1917, 11, 7.

i E. Rimbach and F. Korten, Z. anorg. Chem., 1907, 52, 406.

j Mean value.

TABLE 3.3 Unit cell parameters and calculated lattice energies (U_L) for salts A_2MX_6

Salt	$a/\text{\AA}$	$U_L/\text{kJ mol}^{-1}$
Cs_2ReCl_6	10.260 ^a	-1453
Cs_2ReBr_6	10.685 ^a	-1399
Cs_2PtCl_6	10.215 ^b	-1459
K_2ReCl_6	9.840 ^a	-1506
K_2PtCl_6	9.755 ^b	-1521
K_2PtBr_6	10.270 ^b	-1451
K_2SnCl_6	10.002 ^a	-1488
$(\text{NH}_4)_2\text{PtCl}_6$	9.858 ^b	-1507
$(\text{NH}_4)_2\text{PtBr}_6$	10.370 ^b	-1439
$(\text{NH}_4)_2\text{IrCl}_6$	9.870 ^b	-1505

a From ref. 16.

b R. W. G. Wyckhoff, 'Crystal Structures', 2nd edition, Interscience, New York, 1964, vol. 3.

TABLE 3.4 Single-ion hydration enthalpies (ΔH_{si})
for some MX_6^{2-} anions

Anion	Counter-ion	$\Delta H_{\text{si}}/$ kJ mol^{-1}	Mean $\Delta H_{\text{si}}/$ kJ mol^{-1}	M^{4+} radius ^a / \AA
ReCl_6^{2-}	Cs^+	-846	-837	0.72
ReCl_6^{2-}	K^+	-827		
IrCl_6^{2-}	NH_4^+	-833	-833	0.64
PtCl_6^{2-}	Cs^+	-870	-845	0.65
PtCl_6^{2-}	K^+	-830		
PtCl_6^{2-}	NH_4^+	-834		
SnCl_6^{2-}	K^+	-802	-802	0.71
ReBr_6^{2-}	Cs^+	-784	-784	0.72
PtBr_6^{2-}	K^+	-765	-770	0.65
PtBr_6^{2-}	NH_4^+	-774		

^a B. R. Eggin, 'Chemical Structure and Reactivity',
Macmillan, London, 1972, p. 85.

TABLE 3.5 A comparison of single-ion hydration enthalpies (ΔH_{si}) with ionic radii between several uni- and divalent anions

Univalent anion	Divalent anion	Radius/Å	$\Delta H_{si}/$ kJ mol ⁻¹
ClO_4^-		2.36 ^a	-226 ^d
MnO_4^-		2.40 ^a	-247 ^d
ReO_4^-		3.51 ^{a, b}	-172 ^e
	SO_4^{2-}	2.30 ^a	-1109 ^d
	ReCl_6^{2-}	4.25 ^c	-837 ^e
	ReBr_6^{2-}	4.53 ^c	-784 ^e

a W. E. Dasent, 'Inorganic Energetics', Penguin, 1970, p. 85.

b R. D. Shannon and C. T. Prewitt, Acta Crys., 1969, B25, 925; 1970, B26, 1046. (Estimate of the ionic radius for ReO_4^- is based on a value of the radius of Re(VII) with co-ordination number of 6.)

c N. N. Greenwood, 'Ionic Crystals, Lattice Defects and Non-stoichiometry', Butterworths, 1968, pp. 40 - 41.

d Ref. c, p. 27.

e This work.

TABLE 3.6

Measured anion concentrations and calculated (concentration) solubility products (K_s) for saturated solutions of caesium hexachlororhenate(IV) in binary mixed aqueous solvents at 298.2K; the empirical solvent parameters [E_T^a , S , Y , $g(S)$], mole fraction (x_2), and dielectric constants (D) are listed for each solvent mixture.

Non-aqueous component (% by vol.)	x_2	D^a	E_T^b	S^c	Y^d	$g(S)^e$	$10^5 [ReCl_6^{2-}] / mol\ dm^{-3}$	$10^{13} K_s / mol^3\ dm^{-9}$
Water	1.000	78.50	63.1	0.154	3.493	0	24.72	604.1
40% methanol	0.229	63.42	59.2	0.129	2.391	0.75	5.77	7.7
20% } ethanol	0.072	69.35	60.0	0.144	3.051	0.52	11.67	63.6
40% } ethanol	0.171	58.47	56.6	0.126	2.196	1.00	5.57	6.9
60% } ethanol	0.317	46.44	55.0	0.097	1.124	1.50	3.34	1.5
40% dioxane	0.124	43.84	55.6	0.110	1.945	1.38	9.54	34.8

a J. Timmermans, 'The Physico-Chemical Constants of Binary Systems in Concentrated Solutions', Interscience, London, 1959, vol. 1.

b C. Reichardt, 'Lösungsmittelleffekte in der Organische Chemie', Verlag Chemie, Weinheim, 1968.

c S. Brownstein, Canad. J. Chem., 1960, 38, 1590.

d E. Grunwald and S. Winstein, J. Amer. Chem. Soc., 1948, 70, 846.

e Ref. 9.

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CHAPTER 4

THE KINETICS OF METAL-ION CATALYSED AQUATION OF
HEXAHALORHENATE(IV) ANIONS IN AQUEOUS SOLUTION

CHAPTER 4THE KINETICS OF METAL-ION CATALYSED AQUATION OF
HEXAHALORHENATE(IV) ANIONS IN AQUEOUS SOLUTIONINTRODUCTION

There are many examples of spontaneous aquation of ammine-halide and ammine-pseudo-halide complexes of d^3 and low-spin d^6 transition metal cations quoted in the literature. Such spontaneous aquations are invariably slow, but the rate can be greatly accelerated by the presence of suitable metal cations. Available kinetic data on metal-ion catalysed aquations of d^3 and low-spin d^6 systems include the reaction of the $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ cation with mercury(II),¹ thallium(III)² or silver(I),² of the $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ cation with mercury(II),³ and of the $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$ cation with mercury(II).⁴ For all such catalysed aquations, the effectiveness of the catalyst is determined by the strength of the interaction between the catalyst and the halide ligand that is to be substituted. The extent of the interaction must be closely related to the stability constant of the halo-complex of the metal cation. Hence, one might hope to observe more effective catalysis by those metal cations whose halo-complexes have the higher stability constants.

The aquation of the hexachloro- and hexabromo-complex anions of rhenium(IV), ReCl_6^{2-} and ReBr_6^{2-} , follow a similar pattern to the aforementioned complexes of other kinetically

inert transition metal cations. The spontaneous aquations are very slow at normal temperatures; at 308.2K the first-order rate constants have been estimated as $9 \times 10^{-9} \text{ s}^{-1}$ for the hexachlororhenate(IV) anion and $2 \times 10^{-6} \text{ s}^{-1}$ for the hexabromorhenate(IV) anion in acidic aqueous solution.⁵ In the following chapter, investigation into the mercury(II) catalysed aquation of the hexachlororhenate(IV) anion has been extended from the preliminary results reported by J. Burgess et al.⁵ An extensive study of the metal-ion catalysed aquation of the hexachlororhenate(IV) anion has been attempted; kinetic data are reported for the catalytic activity of mercury(II), thallium(III), indium(III) and cadmium(II) in aqueous solution. Activation parameters have been determined for the mercury(II) and thallium(III) catalysed aquations of the hexachlororhenate(IV) anion. An extension of the mercury(II) investigation was intended, by an examination of its catalytic activity upon the aquation of the hexabromorhenate(IV) anion. However, this experiment proved impractical. An extension of the thallium(III) investigation was carried out instead, by a study of its effectiveness in catalysing the aquation of the hexabromorhenate(IV) anion.

The kinetic data detailed in this work are compared with those for the cobalt(III), chromium(III) and rhodium(III) systems mentioned above. The effectiveness of the various catalysts, with respect to the aquation of the hexachloro- and hexabromorhenate(IV) anions, is examined in relation to the stability constants for the monochloro- and monobromo-complexes of the respective metal cations.

EXPERIMENTAL

Preparation of Complexes

Potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV) were prepared by reducing solutions of potassium perrhenate in hydrochloric and hydrobromic acids respectively, with hypophosphorous acid.⁶ Purification was achieved by recrystallisation from the relevant concentrated hydrohalic acid.

Caesium hexathiocyanatorhenate(IV), $\text{Cs}_2\text{Re}(\text{SCN})_6$, was prepared by fusing potassium hexachlororhenate(IV) with potassium thiocyanate under the stirring action of a stream of nitrogen.⁷ The dark brown mixture obtained was isolated by solvent extraction and filtration, a caesium chloride solution was added and the product was filtered off, washed and vacuum dried.

Catalyst Solutions

Mercury(II) perchlorate was supplied by K and K Laboratories, mercury(II) nitrate by Hopkins and Williams and cadmium(II) perchlorate by Alfa Products. Thallium(III) perchlorate and indium(III) perchlorate solutions were each prepared by stirring thallium(III) oxide and indium(III) oxide respectively in the relevant strength perchloric acid solutions at 323.2K overnight. The solutions were then filtered and the filtrates used for kinetic runs as quickly as possible, followed by analysis for thallium(III) or indium(III).

The thallium(III) perchlorate solution was analysed by addition of excess of potassium iodide to aliquot portions of thallium(III) perchlorate solution. The potassium iodide solution contained sodium bicarbonate, so that air was replaced by carbon dioxide, to prevent aerial oxidation of potassium iodide. The liberated iodine was then titrated against sodium thiosulphate, itself standardised against potassium iodate, using fresh starch solution as an indicator.^{8,9}

The indium(III) perchlorate solution was analysed by addition of excess of EDTA, to aliquot portions of indium(III) perchlorate solution, and sufficient 880 ammonia was added to make the solution alkaline. The excess of EDTA was then back-titrated against a standard solution of nickel ammonium sulphate.¹⁰ Two indicators were used, Murexide and HHSNNA, in two separate analyses.

Kinetics

The most convenient method for the study of the catalysed aquations of the hexachloro- and hexabromo-complexes of rhenium(IV) is spectrophotometry, provided that the complex anions have characteristic absorption maxima with sufficiently large molar extinction coefficients. It was advantageous to study the complex anions in the visible region (750 - 350 nm), rather than the ultra-violet region, because of the very large ultra-violet absorptions of nitrate and perchlorate anions in solution.

All the spectra and all but one of the kinetic runs were carried out in 1 cm cells and were recorded using a Unicam SP 800 A recording spectrophotometer fitted with an SP 825 Series 2 Programme Controller. The cell compartment of the spectrophotometer was thermostatted by circulating water through it from a water bath. The water bath temperature was maintained by the use of a contact thermometer and relay-controlled heater. A calibration curve was plotted between 293.2K and 318.2K, by use of a thermocouple, because of the small discrepancy in temperature between the cell compartment and the water bath. The cadmium(II) and indium(III) catalysed aquations of the hexachlororhenate(IV) anion were so slow that the reaction flasks were thermostatted at 323.2K in a separate bath, with spectrophotometric observation of aliquots at intervals. Periodic checks were made to ensure that no solvent loss by evaporation had taken place.

The main charge-transfer bands for the hexachlororhenate(IV) and hexabromorhenate(IV) anions in the near ultra-violet region are at 283 nm ($\epsilon = 13100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 350 nm ($\epsilon = 9900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) respectively.¹¹ These were the two wavelengths at which decreases in absorption with time were monitored, for all kinetic runs performed on the spectrophotometer.

The one exception to the above method was the investigation of the thallium(III) catalysed aquation of the hexabromorhenate(IV) anion. This aquation was so fast that conventional "slow reaction" techniques could not be used at any reasonable concentration of thallium(III)

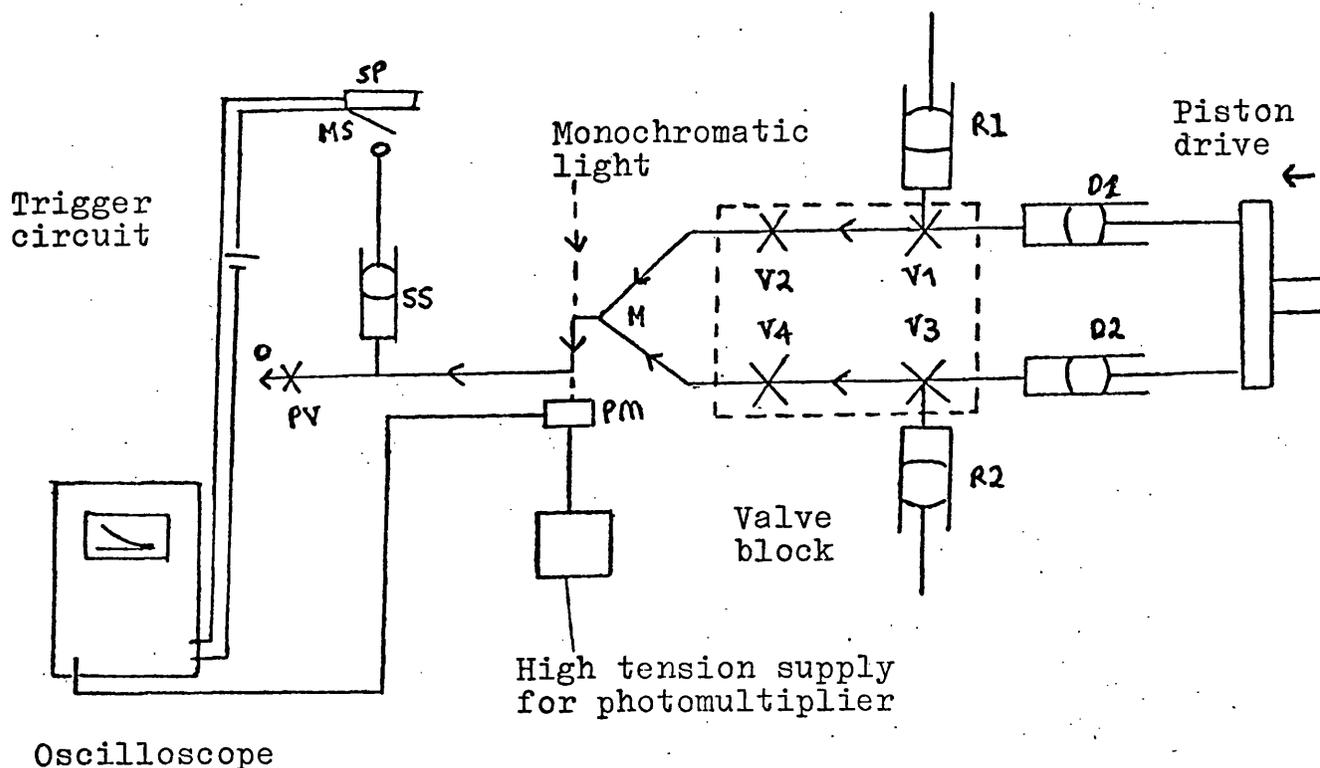
perchlorate. The apparatus used to monitor the reaction consisted of an Applied Photophysics stopped-flow machine¹² (Figure 4.1), which had been linked to the light source and monochromator of a Unicam SP 500 spectrophotometer, a photomultiplier and a storage oscilloscope. The stopped-flow machine was thermostatted, again by use of circulating water drawn from a constant temperature water bath. The main charge-transfer band for the hexabromorhenate(IV) anion in the near ultra-violet region is at 350 nm. Unfortunately, the quantum efficiency of the photomultiplier at 350 nm was about 4%, which was too low to monitor the change in absorption of λ_{max} of the charge-transfer band during the aquation process. Consequently, the spectrophotometer was set at 385 nm, with the slits wide open, to monitor the change in absorption of the shoulder of the 350 nm peak.

All component solutions were thermostatted separately before mixing, for both the conventional "slow reaction" kinetics and the stopped-flow kinetics.

Treatment of Results

The experimental conditions for all the kinetic runs are defined in Table 4.1. For the conventional kinetics, observed first-order rate constants, k_{obs} , were calculated from the decrease in absorption with time, using a standard least-mean-squares programme (see Appendix 3c). The second-order rate constants, k_2 , were computed by the use of a least-mean-squares straight line programme from the dependence of k_{obs} on molar concentration of the catalyst

FIGURE 4.1 Stopped-flow apparatus



KEY

D1 and D2 - hand-driven thermostatted syringes containing components to be mixed

R1 and R2 - reservoir syringes (used to fill D1 and D2 respectively)

V1, V2, V3 and V4 - valves connecting D1 and D2 with R1 and R2 respectively, and connecting D1 and D2 with M

M - mixing chamber

PM - photomultiplier

SS - stopping syringe

MS - micro-switch

SP - stopping-block for micro-switch

PV - valve connecting SS with O

O - outlet for product solution

(Figure 4.2 and Appendix 3d). The slopes of the straight lines gave the k_2 values with standard errors; the intercepts were all shown to be zero.

For each run on the stopped-flow apparatus, the decay curve on the storage oscilloscope was examined to calculate the half-life. When six or more consistent half-lives had been determined for each concentration of thallium(III) perchlorate, an average half-life was calculated. The observed first-order rate constant, k_{obs} , was then calculated from the relationship¹³

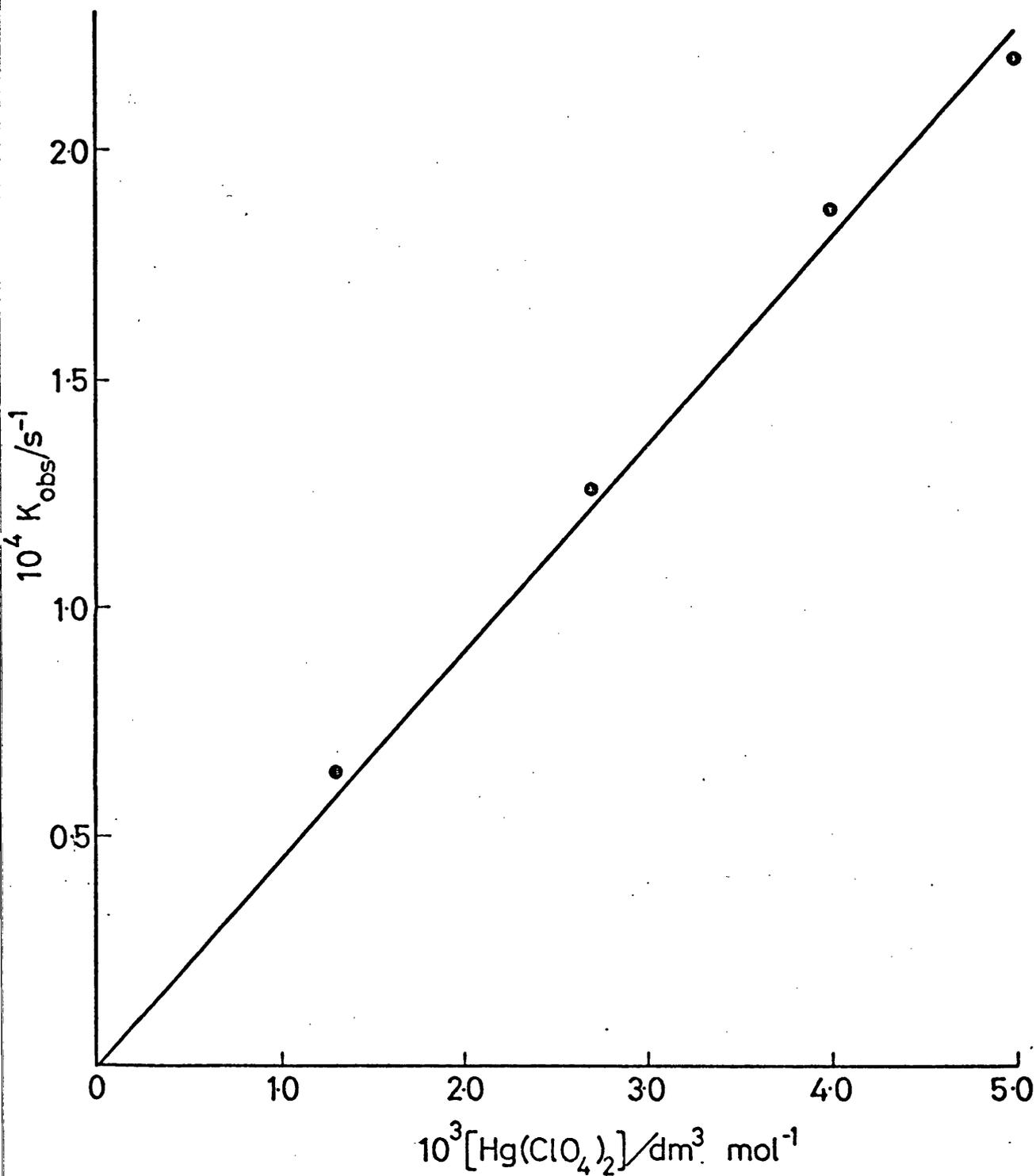
$$k_{\text{obs}} = \frac{\ln 2}{\tau_{1/2}},$$

where $\tau_{1/2}$ is the half-life.

RESULTS

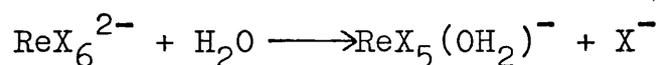
At concentrations of about 10^{-4} mol dm⁻³, both the hexachlororhenate(IV) and hexabromorhenate(IV) anions undergo spontaneous aquation in dilute acidic solutions containing dissolved oxygen.⁵ As the reactions proceed the colours of the solutions fade; the ultra-violet spectra of the product solutions are identical with that reported for perrhenate anions.¹⁴ One cannot tell whether oxidation follows the loss of all six halide ligands from the rhenium(IV) ion, or if it takes place at some earlier stage in the halide-substitution sequence. In the former case, $\text{Re}(\text{H}_2\text{O})_6^{4+}$ would be produced. This species seems not to have been characterised, although a $\text{p}K_1$ value has been reported.¹⁵ $\text{Re}^{4+}(\text{aq})$ is not an

FIGURE 4.2 The dependence of the observed first-order rate constant, k_{obs} , on the molar concentration of mercury(II) perchlorate, $[\text{Hg}(\text{ClO}_4)_2]$, for the catalysed aquation of the hexachlororhenate(IV) anion in aqueous solution at 298.3K



impossible species (cf. $\text{Th}^{4+}_{(\text{aq})}$); indeed, new $\text{M}^{n+}_{(\text{aq})}$ species are still being discovered, for example $\text{Mo}(\text{H}_2\text{O})_6^{3+}$.¹⁶ Of course, the aquated $\text{Re}(\text{IV})$ cation may be in equilibrium in solution with an hydroxo- species such as $\text{Re}(\text{OH})(\text{H}_2\text{O})_5^{3+}$. For the latter case, the $\text{ReCl}_5(\text{OH})^{2-}$ anion is known to oxidise in about the timescale of the hexachlororhenate(IV) spontaneous aquation to perrhenate ion.¹⁷ This and other halohydroxo- or halo-oxorhenate(IV) complexes are known to be considerably more labile than hexahalorhenate(IV) anions. In either case, easy oxidation to the perrhenate anion is known to occur as long as dissolved oxygen is present in solution. Perrhenate anion is also the product obtained in the metal-ion catalysed aquations of the hexachloro- and hexabromorhenate(IV) anions examined in this work.

On consideration of earlier evidence and discussion⁵, it may be assumed that the rate-determining step in the spontaneous aquation involves loss of the first halide ligand from the rhenium(IV) complex anion, i.e.

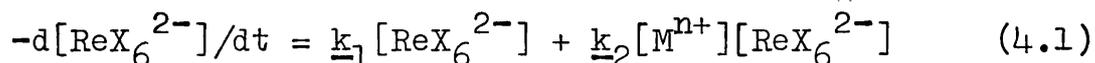


Hence, all the complications discussed in the previous paragraph are irrelevant to the kinetics, because the rate-determining step occurs so early in the overall reaction.

A preliminary scrutiny of the systems available for consideration established those worth a fuller investigation. Silver(I) was unsuitable as a catalyst for aquation of both the chloro- and bromo- anions because of the insolubility of its hexahalorhenate(IV) salts.⁴ Mercury(II) quickly formed a precipitate with the hexabromo-

rhenate(IV) anion and with the pseudo-halide complex anion, hexathiocyanatorhenate(IV). Hence, examination of mercury(II) was limited to its catalytic activity upon aquation of the hexachlororhenate(IV) anion. Thallium(III) was an effective catalyst for both the hexachlororhenate(IV) and hexabromorhenate(IV) anions, producing no precipitates. Thallium(III) catalysed aquation of hexabromorhenate(IV) was too fast to follow by conventional "slow reaction" techniques at any reasonable concentration of thallium(III), but was easily followed by a "stopped-flow" technique.¹⁸ Mercury(II) and thallium(III) were found to have large catalytic effects, indium(III) and cadmium(II) were found to have very small, almost or completely negligible effects.

All kinetic runs were carried out in the presence of a large excess of the metal-ion so that pseudo-first-order conditions were maintained. First-order kinetics were followed for at least three half-lives. The observed rate constants, k_{obs} , for the aquation of the hexachloro- and hexabromorhenate(IV) anions, and their variation with the concentration of metal-ion, are reported in Tables 4.2, 4.3, 4.4 and 4.5. The results can be accommodated by one general rate law for the catalytic aquation by a metal-ion, M^{n+} , shown in equation (4.1).



k_1 is the rate constant for spontaneous aquation.

k_2 is the rate constant for catalysed aquation.

The kinetics of most of the examples of metal-ion catalysed aquations already cited indicate simple second-

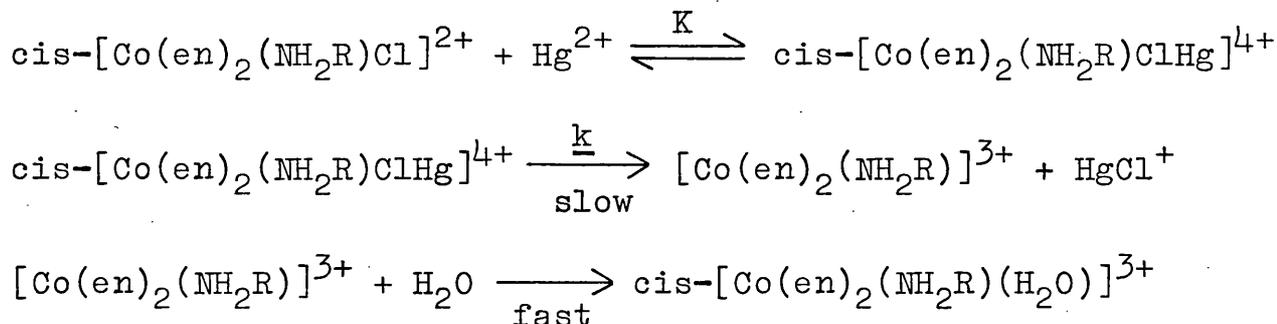
order behaviour. One notable exception is the mercury(II)^{2,19} or thallium(III)^{2,20} catalysed aquation of cobalt(III) complex cations of the type $\text{cis-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$. In this type of system, the apparent second-order rate constant decreases upon increase in concentration of the metal-ion. This deviation from second-order behaviour is explained by a pre-equilibrium association to form a stable binuclear adduct. The rate-determining step involves the unimolecular dissociation of the adduct, with $\text{MX}^{(n-1)+}$ as the leaving group.

From a simple electrostatic approach, formation of a stable intermediate seems more likely for the hexahalo-rhenate(IV)/ M^{n+} system because of the bonding between the oppositely charged ions that would be necessary, ReX_6^{2-} with M^{n+} . The formation of such an intermediate would be governed by the ease of breaking the $\text{Re}^{\text{IV}}\text{-X}$ bond and by the ease of forming the $\text{M}^{n+}\text{-X}$ bond. The effect of differences in bond strengths between $\text{Re}^{\text{IV}}\text{-X}$ and $\text{Co}^{\text{III}}\text{-X}$, for example, upon possible formation of an intermediate, is unknown. For the metal-ion catalysed aquations of the hexahalo-rhenate(IV) anions discussed here, there was no evidence of an intermediate; a plot of the observed rate constant, k_{obs} , against concentration of the metal-ion, $[\text{M}^{n+}]$, gave a straight line (Figure 4.2). However, it should be borne in mind that at high concentrations of M^{n+} such plots might begin to curve, eventually becoming parallel to the M^{n+} concentration axis (cf. References 2 and 19). In practice, it is difficult to work at varying high M^{n+} concentrations while maintaining constant ionic strength.

The results collected together in Tables 4.2 and 4.3 show that for mercury(II) and thallium(III), $k_2[M^{n+}][\text{ReX}_6^{2-}] \gg k_1[\text{ReX}_6^{2-}]$. Under such conditions equation (4.1) effectively reverts to a simple second-order rate law, except at extremely low concentrations of metal-ion. At the other extreme, $k_1[\text{ReX}_6^{2-}] \gg k_2[M^{n+}][\text{ReX}_6^{2-}]$ for indium(III). The spontaneous aquation now makes the only significant contribution to the overall rate and equation (4.1) reverts to a first-order rate law at all accessible concentrations of indium(III). The remaining case is that of cadmium(II) and it belongs to neither extreme; $k_1[\text{ReX}_6^{2-}] \sim k_2[\text{Cd}^{2+}][\text{ReX}_6^{2-}]$ at the concentrations used. The cadmium(II) results in Table 4.4 indicate a value for k_1 of $3 \times 10^{-6} \text{ s}^{-1}$ at 323.2K, which agrees well with the value for k_1 of between 3 and $4 \times 10^{-6} \text{ s}^{-1}$ at 323.2K for the indium(III) experiments. One would like to compare these k_1 values with k for a spontaneous aquation experiment. Unfortunately, this cannot be done very satisfactorily. The only published results on the kinetics of spontaneous aquation of the hexachlororhenate(IV) anion⁵ give a very approximate estimate of $k \sim 10^{-8} \text{ s}^{-1}$ at 308.2K. The above k_1 values on the cadmium(II) and indium(III) experiments are not inconsistent with this published value, assuming a reasonable estimate for the activation enthalpy for spontaneous aquation.

As mentioned earlier, the kinetics of aquation of several cobalt(III)-chloride¹⁹ and rhodium(III)-chloride⁴ complexes catalysed by mercury(II) ions exhibit deviations from the more common second-order kinetics. Both the straightforward and the more unusual kinetics observed are explained by the authors in terms of an equilibrium association of the

MA_5Cl^{n+} complex cation with the mercury(II) cation, to form a binuclear intermediate, M-Cl-Hg. The following step is a rate-determining "unimolecular" dissociation of the intermediate to give the aquated product and $HgCl^+$; for example, from Reference 19,



Under pseudo-first-order conditions, the observed rate constant is given by

$$k_{\text{obs}} = kK[Hg^{2+}]$$

It is believed that the lead(II) catalysed elimination of chloride ion from cis-chlorobis(ethylene-diamine)glycinato-N-cobalt(III), $cis-[Co(en)_2(NH_2CH_2COO)(Cl)]^+$, also goes via an intermediate in the major reaction path.²¹ However, there is evidence that the association is primarily with the free carboxylate group and not the chloride ligand alone.

There is some disagreement in the literature concerning the thallium(III) catalysed aquations of cobalt(III)-chloride complexes. A. G. Sykes et al.² maintain that the extra positive charge, when using thallium(III) instead of mercury(II) in the metal-ion catalysed aquation of $cis-[Co(en)_2Cl_2]^+$, reduces the extent of association between the catalyst and the complex cation. This leads to the saturation of the pre-

equilibrium, to form a stable binuclear adduct, $\text{cis-}[\text{Co(en)}_2\text{Cl}_2\text{Tl}]^{4+}$, being kinetically unobservable. Chan and Chan,²⁰ however, point out that two interpretations of the one mechanism are possible to account for the deviation from second-order kinetics of the thallium(III) catalysed aquation of $\text{cis-}[\text{Co(en)}_2(\text{RNH}_2)\text{X}]^{2+}$. Both interpretations involve formation of an intermediate of the form, $\text{cis-}[\text{Co(en)}_2(\text{RNH}_2)(\text{TlX})]^{5+}$. The authors cannot decide which interpretation to favour.

The kinetics of the $\text{ReX}_6^{2-}/\text{M}^{n+}$ systems show a linear dependence of rate on the molar concentration of M^{n+} , when M^{n+} is mercury(II), thallium(III) and cadmium(II). The linear dependence is consistent with a direct rate-determining associative attack of M^{n+} at the ligand, but an $\text{S}_{\text{E}}2$ attack at the catalytic cation, M^{n+} . The kinetics are also consistent with a pre-equilibrium association to give a stable binuclear intermediate followed by a rate-determining unimolecular dissociation with $\text{MX}^{(n-1)+}$ as the leaving group. The second possibility requires a low equilibrium constant for formation of the intermediate. The kinetics are not consistent with rapid and almost complete formation of the intermediate followed by slow dissociation.

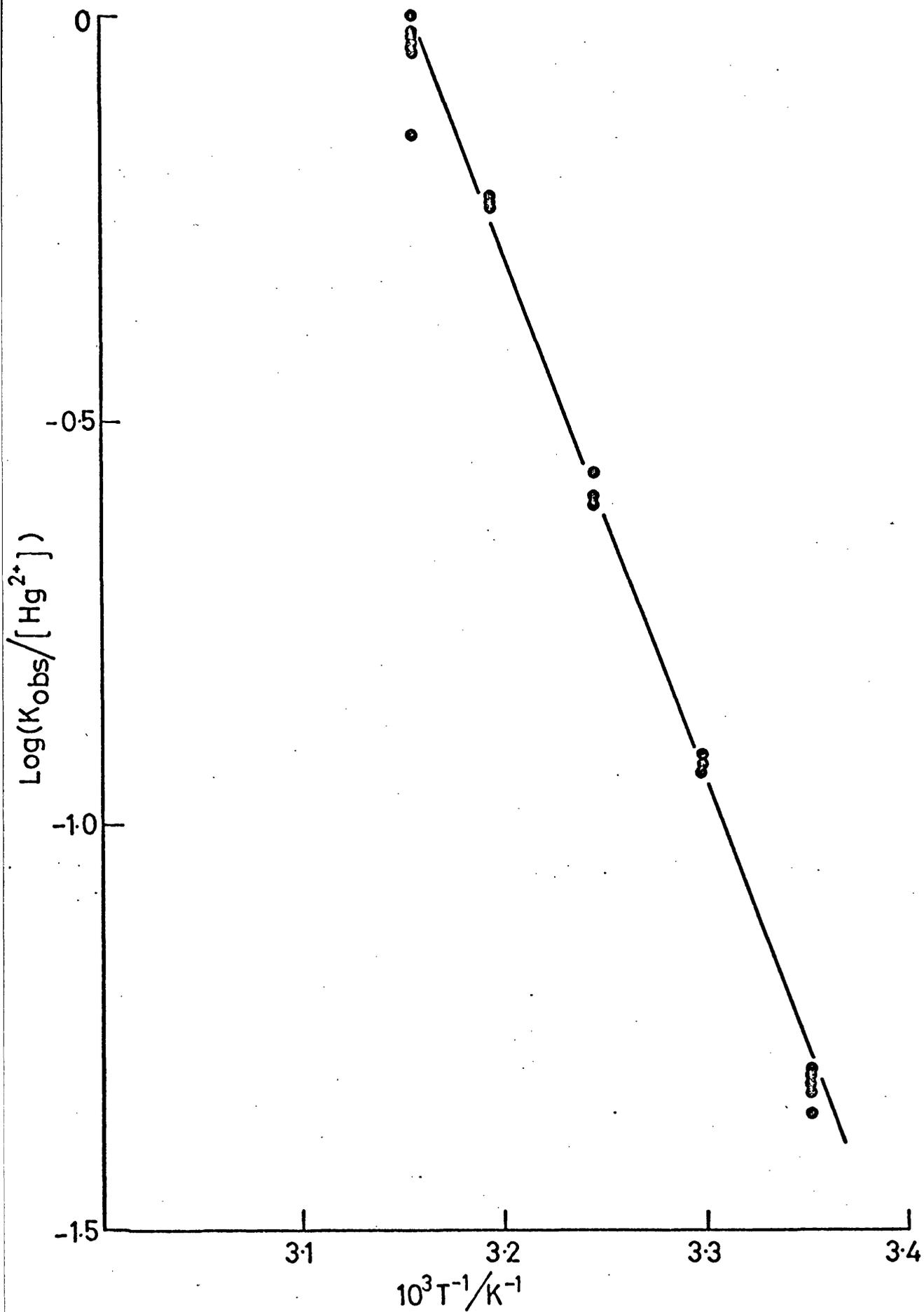
In the analysis of the results for the present work, it seemed most reasonable to work on the simplest assumption, that the bimolecular associative attack of M^{n+} at the halide ligand is the rate-determining step, i.e. k_2 of equation (4.1) is a simple bimolecular rate constant. One must bear in mind, however, that this k_2 , and the activation parameters derived therefrom, may be composite quantities, with part of the

reaction progressing via equilibrium formation of an intermediate. Values of k_2 and their standard errors, computed from the k_{obs} values by a standard least-mean-squares programme (Appendix 3d), are given in Tables 4.2, 4.3, 4.4 and 4.5.

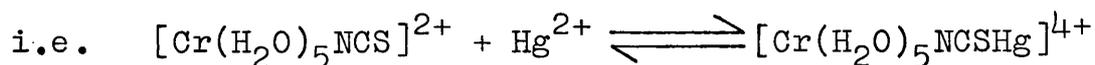
Activation parameters were determined where possible from the rate constants in Tables 4.2 and 4.3, and are reported in Table 4.7. The Table 4.7 values with their standard errors were computed with a least-mean-squares programme from the dependence of the decadic logarithm of the $(k_{\text{obs}}/[M^{n+}])$ quotient on $\frac{1}{T}$. The intercept is the logarithm of the A factor and the slope is $-(E_a/2.303RT)$. The quotient, $(k_{\text{obs}}/[M^{n+}])$, was taken for each value of k_{obs} in Tables 4.2 and 4.3. A typical Arrhenius plot is illustrated in Figure 4.3 for the mercury(II) catalysed aquation of the ReCl_6^{2-} anion.

For all but one of the systems studied herein, the catalysts were used in the form of the perchlorate salts (in perchloric acid solution), to keep complex formation between M^{n+} and anions to a minimum. Under such conditions, one may consider the catalytic species as simply $M^{n+}(\text{aq})$. For the hexachlororhenate(IV) catalysed aquation by mercury(II), an attempt was made to obtain some supportive data by using mercury(II) nitrate in nitric acid solution. Surprisingly, the consistency of the results was poorer and the rate constants were slightly lower than for the analogous experiments with mercury(II) perchlorate in perchloric acid solution. Typically, six or seven determinations of a given rate constant varied between the value obtained in perchlorate media and about one-half of that value (Table 4.2).

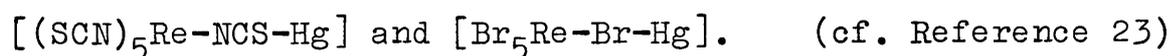
FIGURE 4.3 Plot of logarithms of ($k_{\text{obs}}/[\text{Hg}^{2+}]$) quotient 111 against reciprocal temperature for the mercury(II) catalysed aquation of the hexachlororhenate(IV) anion



The mercury(II) catalysed aquations of cobalt(III) and chromium(III) pseudo-halide complexes have been previously studied. The isothiocyanatopenta-aquochromium(III) complex cation, $[\text{Cr}(\text{H}_2\text{O})_5\text{NCS}]^{2+}$, is one of many that rapidly produces a stable binuclear intermediate in the presence of a large excess of mercury(II) ions.²²



It seemed possible that one might observe the kinetics of reaction of the hexathiocyanatorhenate(IV) anion with mercury(II). Unfortunately, upon mixing excess of mercury(II) perchlorate solution with the hexathiocyanatorhenate(IV) solution, immediate precipitation occurred, as in the case of the hexabromorhenate(IV) anion with mercury(II). It is likely that these precipitates are neutral bimetallic species of the form,

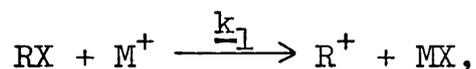


DISCUSSION

A study of the rate constants collected together in Table 4.6 enables an assessment to be made of the effectiveness of mercury(II) as a catalyst for the aquation of $\text{Re}^{\text{IV}}-\text{Cl}$, $\text{Co}^{\text{III}}-\text{Cl}$, $\text{Cr}^{\text{III}}-\text{Cl}$ and $\text{Rh}^{\text{III}}-\text{Cl}$. The results suggest that mercury(II) exhibits the strongest aquation catalysis for rhenium(IV)-chloride. Unfortunately, it is not possible to make analogous assessments on the effectiveness of thallium(III) and cadmium(II) aquation catalysts for the same range of

compounds because of the lack of appropriate kinetic results. It does appear, however, that thallium(III) is a more effective catalyst for the aquation of $\text{Re}^{\text{IV}}\text{-Cl}$ than for the aquation of $\text{Co}^{\text{III}}\text{-Cl}$. Even more unfortunately, it is not possible to compare the mercury(II) and thallium(III) results in Table 4.6 with the catalytic effect of these same metal-ions upon the solvation of C-Cl.

There is an extensive correlation of solvolysis rate constants with metal complex stability constants for the metal-ion catalysed solvolysis of t-butyl chloride in 32 wt.% ethanol-water at 298.2K in the literature.²⁴ However, the authors found the catalytic activities of mercury(II) and thallium(III) too high to measure by their methods, and catalytic data for indium(III) are not included. The authors found that C-X bond heterolysis ($\text{S}_{\text{N}}1$ mechanism) due to the reaction,



is accelerated by metal-ions, M^+ (Lewis acids), which form stable halide complexes, MX, with reagent X^- . The rate law found was

$$-d[\text{RX}]/dt = k_0[\text{RX}] + k_1[\text{M}^+][\text{X}^-]$$

where k_0 is the rate constant of the RX (t-butyl chloride in this case) solvolysis in the same solvent. The authors proposed a Brønsted type equation connecting k_1 , k_0 and the stability constant of the complex, $K = [\text{MX}]/[\text{M}^+][\text{X}^-]$, viz.

$$\log(k_1/k_0) = -0.7 + 0.84 \log K \quad (4.2)$$

which covers all variations of metal, RX halide and solvent.

From the graph plotted of $\log(k_1/k_0)$ against $\log K$, it is possible to estimate a value of (k_1/k_0) for the catalytic effect of cadmium(II) upon the solvolysis of t-butyl chloride in 32 wt.% ethanol-water at 298.2K.

$$\log(k_1/k_0) \approx 1$$

$$\therefore (k_1/k_0) \approx 10$$

Interpolation of the rates of solvolysis of t-butyl chloride at 298.2K in ethanol-water mixtures, given in the literature,²⁵ produced an estimate of the solvolysis rate constant, k_0 , in 27 vol.% (32 wt.%) ethanol-water of $643 \times 10^{-5} \text{ s}^{-1}$. Hence, $k_1 \approx 6 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

(k_1/k_0) values for the cadmium(II) catalysed solvolysis of t-butyl chloride in 32 wt.% ethanol-water and (k_2/k_1) for the cadmium(II) catalysed aquation of the hexachlororhenate(IV) anion in water, both at 298.2K, are 10 and $0.0006 \text{ dm}^3 \text{ mol}^{-1}$ respectively. Although such a comparison must be regarded warily, because of the different media involved, it does appear that cadmium(II) catalytic activity is stronger for C-Cl than $\text{Re}^{\text{IV}}\text{-Cl}$ solvolysis.

A more recent publication by the same authors²⁶ illustrates that equation (4.2) is also approximately valid for the metal-ion catalysed aquation of octahedral cobalt(III), chromium(III) and rhodium(III) halo-complexes. In the case of charged reagents they argue that equation (4.2) must include a term corresponding to the coulombic interaction.

$$\log(k_1/k_0) = -0.7 + 0.84 \log K - CZ_1Z_2$$

where Z_1 and Z_2 are the charges of the complex and of the metal-ion respectively.

The low catalytic activity of indium(III) in this work is in line with some earlier qualitative work by Sykes et al.² The authors report that the catalytic activities of cadmium(II), indium(III) and iron(III) cations are much weaker than those of mercury(II) and thallium(III) for the metal-ion catalysed aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$.

The activation enthalpies of the mercury(II) catalysed aquation of the $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$, $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ cations are 14.6, 35.1 and 35.6 kJ mol^{-1} respectively lower than the activation enthalpies for the spontaneous aquation (Table 4.7). Knowing that the activation enthalpy for the mercury(II) catalysed aquation of the hexachlororhenate(IV) anion is 123.0 kJ mol^{-1} , one can hazard a guess that the activation enthalpy for the spontaneous aquation of the hexachlororhenate(IV) anion lies between 138 and 159 kJ mol^{-1} . This is much higher than the value of 108.8 kJ mol^{-1} determined for the spontaneous aquation of the hexabromorhenate(IV) anion.⁵ Such a large difference of around 29 - 50 kJ mol^{-1} between chloro- and bromo- complexes is unusual. For the hexachloroiridate(III) and hexabromo-iridate(III) anions the difference is 20.5 kJ mol^{-1} , and for $[\text{M}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{M}(\text{NH}_3)_5\text{Br}]^{2+}$ cations, with $\text{M} = \text{Co}$,²⁷ Rh ^{4,27} and Cr ,²⁷ the difference is 4.2, 4.2 and zero kJ mol^{-1} respectively.

Mercury(II) is more effective than thallium(III) for the metal-ion catalysed aquation of the hexachlororhenate(IV) anion. A similar magnitude effect occurs for the metal-ion catalysed aquation of the $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ cation, i.e.

$$\underline{k}_2(\text{Hg}^{2+})/\underline{k}_2(\text{Tl}^{3+}) = 8.7 \text{ for } \text{ReCl}_6^{2-} \text{ at } 308.2\text{K}$$

$$\underline{k}_2(\text{Hg}^{2+})/\underline{k}_2(\text{Tl}^{3+}) = 16.2 \text{ for } [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \text{ at } 308.2\text{K}$$

The stronger catalytic effect of mercury(II) over thallium(III) in such aquations has been attributed to the charge and size of the metal-ion² and to the charge product.²⁶ However, mercury(II) and thallium(III) ionic radii are 1.10 and 0.95Å respectively;²⁸ hence, the observation that mercury(II) is a more effective aquation catalyst than thallium(III) is not in accord with a dependence upon the cation radius or upon the charge effects. A later investigation showed that the lead(II) catalysed eliminations of chloride from positive and negative complex ions of $\text{Co}^{\text{III}}\text{-Cl}$ complexes²¹ have almost the same rates. This result, combined with the present $\text{ReX}_6^{2-}/\text{M}^{\text{n}+}$ results, makes one even more wary of the credibility of the explanation by Sykes et al.² The argument by Sykes et al. would be reasonable for the mercury(II) and thallium(III) catalysed aquations of positive complex ions in which pre-equilibrium association occurs. In such cases the catalytic activity of mercury(II) would be greater than that of thallium(III), because the extra positive charge of thallium(III) would reduce the extent of association between the metal-ion and the positive complex ion.

Activation parameters for comparison of the mercury(II) and thallium(III) catalysed aquations of ReX_6^{2-} and $\text{M}(\text{NH}_3)_5\text{Cl}^{2+}$ are shown in Table 4.7. Chan and Chan²⁰ showed that the relative effectiveness of thallium(III) and mercury(II) in the metal-ion catalysed aquation of $\text{Co}^{\text{III}}\text{-Cl}$ is dominated

by the activation entropies, ΔS^\ddagger , while the activation enthalpies, ΔH^\ddagger , remain virtually the same within experimental error. For the metal-ion catalysed aquation of $\text{Re}^{\text{IV}}\text{-Cl}$, the relative effectiveness of the same two catalysts also appears to be dominated by activation entropies, although the disparity in ΔS^\ddagger is not so pronounced as in the $\text{Co}^{\text{III}}\text{-Cl}$ catalysed aquation. These rationalisations are presumably tied up with the greater solvation of thallium(III) than mercury(II) in the ground state and hence the greater change in entropy on moving to the transition state.

Laidler²⁹ quotes an equation to calculate approximate values of ΔS^\ddagger for the reaction between two moieties, A and B, in aqueous solution, viz.

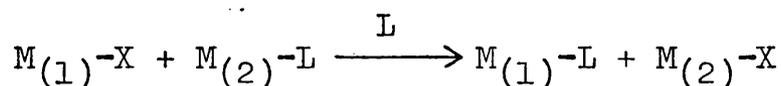
$$\Delta S^\ddagger = - \frac{10Z_A Z_B}{d_{AB}}$$

where Z_A and Z_B are the charges on the reacting species and d_{AB} is the distance between their centres in the activated complex. Estimates of ΔS^\ddagger using this approximation are included, where possible, in Table 4.7. The major discrepancies between the experimental and calculated values of ΔS^\ddagger occur in the $\text{ReCl}_6^{2-}/\text{Hg}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}/\text{Tl}^{3+}$, $\text{cis-Coen}_2(\text{MeNH}_2)\text{Cl}^{2+}/\text{Hg}^{2+}$ and $\text{cis-Coen}_2(\text{MeNH}_2)\text{Cl}^{2+}/\text{Tl}^{3+}$ systems. It is hard to understand the large discrepancy for the $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}/\text{Tl}^{3+}$ system. The discrepancies between experimental and calculated ΔS^\ddagger values for the $\text{ReCl}_6^{2-}/\text{Hg}^{2+}$ and $\text{cis-Coen}_2(\text{MeNH}_2)\text{Cl}^{2+}/\text{Hg}^{2+}$ systems are similar in the sense that whereas the experimental value is more positive for the $\text{ReCl}_6^{2-}/\text{Hg}^{2+}$ system, it is less negative for the $\text{cis-Coen}_2(\text{MeNH}_2)\text{Cl}^{2+}/\text{Hg}^{2+}$ system. Although such a comparison

of mercury(II) catalysed aquations of positive and negative complexes is dubious, it may create a little doubt about the simple second-order kinetics of the mercury(II) catalysed aquation of the hexachlororhenate(IV) anion. Suffice it to say that the comparison allows for the possibility of some pre-equilibrium association in the mercury(II) catalysed aquation of the hexachlororhenate(IV) anion. In such circumstances, the k_2 values and the activation parameters determined would be composite quantities as mentioned earlier.

The relation between the rate constants for the metal-ion catalysed aquation of the hexahalorhenate(IV) complex anions and the stability constants for the respective monohalo- complexes of the metal-ion catalyst is detailed in Table 4.8 and illustrated in Figure 4.4. Unfortunately, a single definitive stability constant appropriate to the conditions of this work cannot be quoted, as the values given in the standard source³⁰ are for a variety of conditions. Moreover, the values given in this source themselves vary over a wide range. Hence, the range of stability constants for each monohalo- complex is simply quoted in Table 4.8. One would be happier if the correlation depicted in Figure 4.4 could be made more explicit by obtaining more points for this plot. It was with this idea in mind that further approaches to the problem of finding more suitable cations were examined.

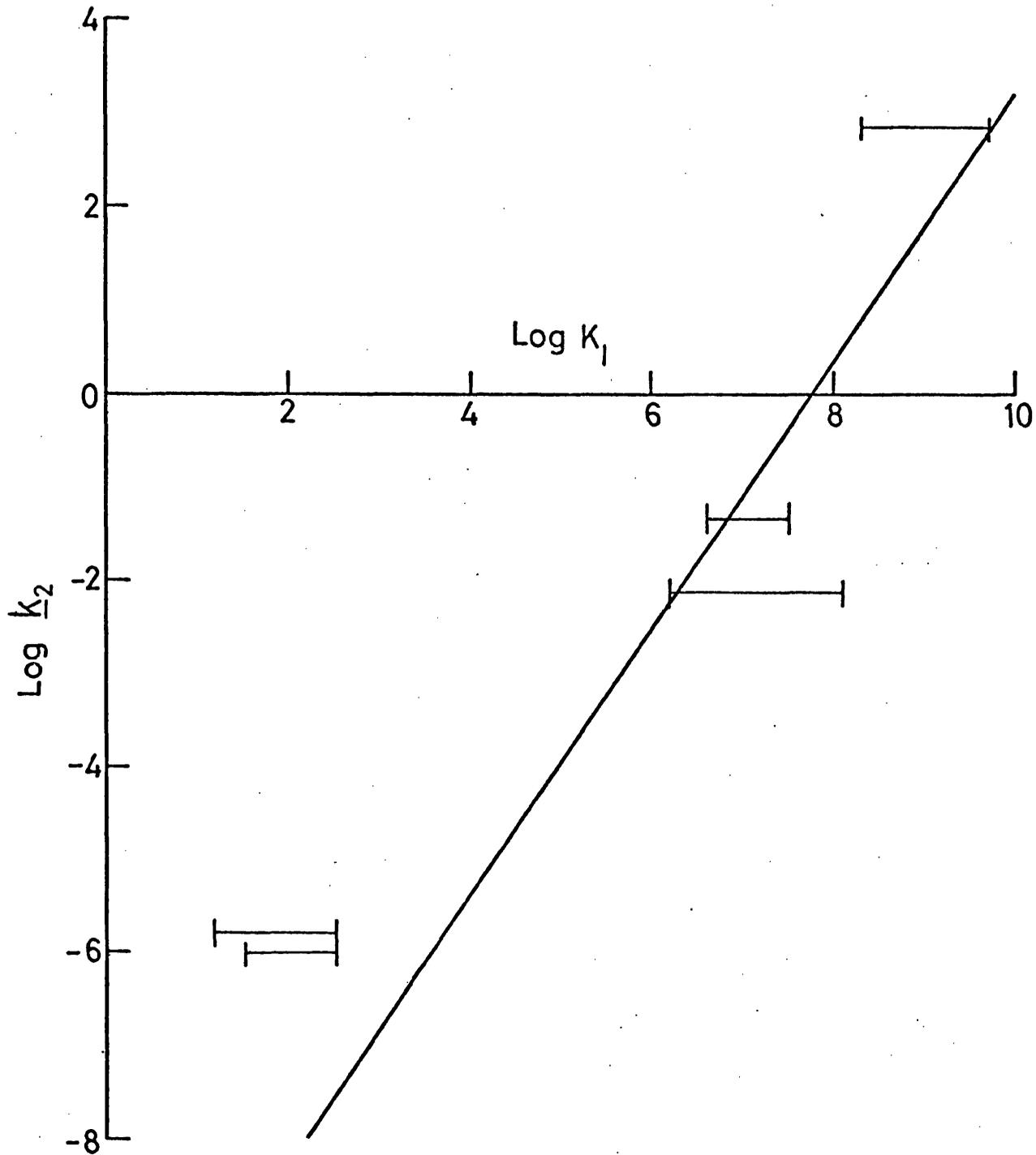
Jones and Clark³¹ extended Pearson's³² notion concerning the rates of ligand substitution reactions, i.e.



where $M_{(1)}$ and $M_{(2)}$ are Lewis acids, X and L are Lewis bases

FIGURE 4.4

Dependence of the logarithm of the second-order rate constant, $\log k_2$, upon the logarithm of the stability constant of the monohalo-complex, $\log K_1$, of the catalytic metal-ion



and $M_{(2)}$ is present in a labile complex. The authors argue that the rates should correlate with the acid-base characteristics of the central atom and the exchanged groups to metal-ion assisted and metal-ion catalysed ligand substitution processes. Using this "Hard and Soft Acid-Base Principle", it might be possible to predict which metal cations (Lewis acids) would catalyse displacement of chloride and bromide ions (Lewis bases) from kinetically inert complexes. $Th^{4+}(aq)$, $Zr^{4+}(aq)$, $Ti^{4+}(aq)$, $Al^{3+}(aq)$, $Fe^{3+}(aq)$, $Cu^{2+}(aq)$ and $Be^{2+}(aq)$ are too hard and would be better suited to catalysing the displacement of fluoride rather than chloride or bromide ions. $Pb^{2+}(aq)$ could be used for catalytic displacement of chloride but both $PbCl^+$ and $SnCl^+$ have significantly lower stability constants than $CdCl^+$ and $InCl^{2+}$.

Tanner and Higginson³³ have made a study of the kinetics of elimination of chloride ion from chloro(ethylenediamine-triacetoacetate)cobaltate(III), $Co(Y)Cl^{2-}$, catalysed by trivalent cations. The authors believe, having allowed for the affinity of the catalyst for carboxylate and chloride, that the type of association is the most significant factor to be considered in interpreting catalytic activity. They do admit that the charge and size of the metal cation may also affect catalytic activity. The most interesting feature of this work is the evidence that catalysis by cations can occur through both inner-sphere and outer-sphere association with the $Co(Y)Cl^{2-}$ substrate. Owing to the two sites of activation, their system does not seem the most suitable for such an investigation of differences in catalytic activity.

The work does suggest that where bond polarisation is the dominant feature of a catalysis, as is probable in the catalysis

of aquation of a substitution-inert chloro-complex, then outer-sphere interactions seem unlikely to lead to pronounced catalysis. In reactions where the principal effect of a catalyst is to bring together two similarly charged species, the authors suggest that fairly strong outer-sphere catalysis should be possible. The authors include a graph, in which $\log k_1$ is plotted against $(\log K_A + \log K_C)$, where K_A is the first association constant for the catalyst cation with acetate and K_C is the first association constant for the catalyst cation with chloride. A study of this plot shows the much stronger catalytic activity of thallium(III), mercury(II) and indium(III) than any of the other cations examined.

As mentioned earlier, investigation of silver(I) catalysis was precluded by the insolubility of the Ag_2ReX_6 salts. The stability constant for formation of PdCl^+ is about 6. $\text{Pd}^{2+}(\text{aq})$ would thus seem a likely candidate for examination of its catalytic activity, although its very different geometry compared to $\text{Hg}^{2+}(\text{aq})$, $\text{Tl}^{3+}(\text{aq})$ and $\text{Cd}^{2+}(\text{aq})$ makes it look less attractive. Stability constants of $\text{CrCl}^{2+}(\text{aq})$, $\text{FeCl}^{2+}(\text{aq})$, $\text{PtCl}^{3+}(\text{aq})$ and $\text{ZnCl}^+(\text{aq})$ are all lower than 1 and the corresponding $\text{M}^{n+}(\text{aq})$ metal-ion catalytic activity would be weaker than even $\text{Cd}^{2+}(\text{aq})$ in all four cases.

The much stronger catalytic activity of mercury(II) compared to thallium(III) in the hexahalorhenate(IV) work and in the other systems cited, where pre-equilibrium association is negligible, throws a great deal of doubt upon the idea that charge and size control the catalytic

activity. The difference in catalytic activity between mercury(II) and thallium(III) cannot be charge controlled because their relative effectiveness is similar for the aquation of the ReCl_6^{2-} and Co-Cl^{n+} complex ions. The extent of X-M^{n+} bond formation and its strength play the major rôle in controlling catalytic effectiveness, not the charge of the halide-containing complex ion. This argument is borne out by the close relation between the catalytic effectiveness of the metal-ion and the stability constant of the monohalo-complex of the metal-ion (Figure 4.4).

CONCLUSION

The rates of the metal-ion, M^{n+} , catalysed aquation of the hexachlororhenate(IV) and hexabromorhenate(IV) anions in acid aqueous solution have been studied. The results are all accommodated by a two-term rate law,

$$-d[\text{ReX}_6^{2-}]/dt = k_1[\text{ReX}_6^{2-}] + k_2[\text{M}^{n+}][\text{ReX}_6^{2-}]$$

Rate constants have been determined for the aquations catalysed by mercury(II) (Table 4.2), thallium(III) (Table 4.3), cadmium(II) and indium(III) ions (Table 4.4).

Activation parameters have been derived for the mercury(II) and thallium(III) catalysed aquations of the hexachlororhenate(IV) anion (Table 4.7). The cadmium(II) and indium(III) catalysed aquations of the hexachlororhenate(IV) anion were too slow to derive activation parameters, while the thallium(III) catalysed aquation of the hexabromorhenate(IV) anion was too fast to derive activation parameters.

The results have been compared with those for similar systems and it has been suggested that the effectiveness of the catalysts bears a direct relation to the stability constants of the monohalo- complexes of the respective metal cations.

TABLE 4.1 Experimental conditions for all kinetic runs

System	$10^5 [\text{ReX}_6^{2-}] / \text{mol dm}^{-3}$	$10^3 [\text{M}^{n+}] / \text{mol dm}^{-3}$	$[\text{H}^+] / \text{mol dm}^{-3}$	<u>Ia</u>	Added Salt
$\text{ReCl}_6^{2-} / \text{Hg}^{2+}$	5.4	1.3-5.0	0.05	0.065	NaClO_4
$\text{ReCl}_6^{2-} / \text{Tl}^{3+}$	5.4	2.0-7.5	1.25	1.25	
$\text{ReCl}_6^{2-} / \text{Cd}^{2+}$	5.3	250-500	2.5	4.5	NaClO_4
$\text{ReCl}_6^{2-} / \text{In}^{3+}$	5.4	220-560	2.5	2.5	
$\text{ReBr}_6^{2-} / \text{Tl}^{3+}$	7.5	3.5-13.8	3.0	3.0	

a Ionic strength.

TABLE 4.2 Observed first-order rate constants, k_{Obs} , and derived second-order rate constants, k_2 , for the mercury(II) catalysed aquation of the hexachlororhenate(IV) anion in aqueous solution

$10^3 [\text{Hg}(\text{ClO}_4)_2] / \text{dm}^3 \text{ mol}^{-1}$	$10^4 k_{\text{Obs}} / \text{s}^{-1}$					$k_2 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
	1.3	2.7	4.0	5.0		
298.3K	0.64	1.26	1.87	2.2	0.045 ± 0.002	
298.3K	0.65	1.29	1.90	2.2	0.044 ± 0.002	
303.2K	1.55	3.3	4.7	5.8	0.177 ± 0.002	
308.2K	3.3	7.4	10.2	12.6	0.26 ± 0.01	
313.1K	7.7	16.2	24	29	0.59 ± 0.01	
317.0K	11.9	19.3	40	48	0.98 ± 0.09	
317.0K	12.2	27	37	45	0.92 ± 0.03	
$10^3 [\text{Hg}(\text{NO}_3)_2] / \text{dm}^3 \text{ mol}^{-1}$	1.3	2.7	4.0	5.0		
293.9K	0.18-0.36	0.36-0.72	0.51-1.12	0.48-1.52	0.015	
299.1K	0.20-0.68	0.76-1.10	1.17-1.47	1.33-1.78	0.028	
303.6K	0.72-1.20	1.53-1.94	2.30-3.27	2.82-3.96	0.062	
307.8K	1.60-2.85	2.91-3.77	4.02-5.69	6.35-8.09	0.135	
312.4K	3.15-5.20	6.85-9.00	7.47-12.40	11.92-17.39	0.280	
316.8K	5.06-10.44	12.06-16.0	16.00-26.90	14.37-35.00	0.510	

TABLE 4.3 Observed first-order rate constants, k_{obs} , and derived second-order rate constants, k_2 , for the thallium(III) catalysed aquation of the hexachlororhenate(IV) anion in aqueous solution

$10^3 [\text{Tl}(\text{ClO}_4)_3] / \text{mol dm}^{-3}$	$10^4 k_{\text{obs}} / \text{s}^{-1}$			$k_2 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
	2.0	4.0	6.0	7.5
297.0K			0.33	0.50
297.1K			0.42	0.66
304.3K			1.04	1.51
309.0K	0.76	1.12	1.85	2.5
314.1K	1.50	3.4	4.9	6.5
314.3K	1.82	3.9	6.0	7.4
319.4K	3.3	6.7	10.5	13.2
319.5K	3.9	8.4	12.3	15.5
				0.032 ± 0.004
				0.089 ± 0.004
				0.102 ± 0.002
				0.181 ± 0.003
				0.21 ± 0.004

TABLE 4.4 Observed first-order rate constants, k_{obs} , and derived second-order rate constants, k_2 , for cadmium(II) and indium(III) catalysed aquations of the hexachlororhenate(IV) anion in aqueous solution

	$10^4 k_{obs} / s^{-1}$		$k_2 / dm^3 mol^{-1} s^{-1}$
$10^3 [Cd(ClO_4)_2] / mol dm^{-3}$	250	375	0.0000016 ± 0.1 × 10 ⁻¹³
	0.007	0.009	
	0.011	0.011	
$10^3 [In(ClO_4)_3] / mol dm^{-3}$	220	330	0
	0.004	0.003	
	0.003	0.003	

TABLE 4.5 Observed first-order rate constants, k_{obs} , and derived second-order rate constants, k_2 , for thallium(III) catalysed equation of the hexabromorhenate(IV) anion in aqueous solution

$10^3[\text{Tl}(\text{ClO}_4)_3]/\text{mol dm}^{-3}$	$k_{\text{obs}}/\text{s}^{-1}$		$k_2/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
	3.5	6.9	13.8
300.2K	1.35	4.5	780 \pm 60 ^a
		7.4	9.4

^a cf. At 300.2K, $k_2(\text{ReCl}_6^{2-}/\text{Hg}^{2+}) \approx 0.0103$ from interpolation

TABLE 4.6 A comparison of the effectiveness of mercury(II) and thallium(III) as catalysts for the aquation of various chloride complexes

Catalyst	Complex(temp/K)	k_2 (M ⁿ⁺ -catalysed) / dm ³ mol ⁻¹ s ⁻¹	k_1 (spontaneous) / s ⁻¹	$\frac{k_2}{k_1}$ / dm ³ mol ⁻¹	Reference
Mercury(II)	ReCl ₆ ²⁻ (308.2)	0.26	9x10 ⁻⁹	290x10 ⁵	This work
	ReCl ₆ ²⁻ (323.2)	2.41 ^a	3.5x10 ⁻⁵	7x10 ⁴	This work
	Co(NH ₃) ₅ Cl ²⁺ (308.2)	0.55	6.0x10 ⁻⁶	0.92x10 ⁵	<u>b</u>
	cis-Coen ₂ Cl ₂ ⁺ (298.2)	200	2.4x10 ⁻⁴	8.3x10 ⁵	<u>c, d</u>
	trans-Coen ₂ Cl ₂ ⁺ (298.2)	3.8	3.5x10 ⁻⁵	1.06x10 ⁵	<u>c, d</u>
	Rh(NH ₃) ₅ Cl ²⁺ (298.2)	2.3x10 ⁻⁴	1.5x10 ⁻⁸	0.15x10 ⁵	<u>e</u>
		6.1x10 ⁻⁴	8.6x10 ⁻⁸	0.07x10 ⁵	<u>f</u>
	Cr(NH ₃) ₅ Cl ²⁺ (298.2)	8.7x10 ⁻²	7.3x10 ⁻⁶	0.12x10 ⁵	<u>b, c, g</u>

contd....

TABLE 4.6 (contd.)

Catalyst	Complex(temp/K)	$\frac{k_2}{k_1}$ (M ⁿ⁺ -catalysed) / dm ³ mol ⁻¹ s ⁻¹	$\frac{k_1$ (spontaneous) / s ⁻¹	$\frac{k_2}{k_1}$ / dm ³ mol ⁻¹	Reference
Thallium(III)	ReCl ₆ ²⁻ (308.2)	0.03	9x10 ⁻⁹	33x10 ⁵	This work
	Co(NH ₃) ₅ Cl ²⁺ (308.2)	0.034	6x10 ⁻⁶	0.057x10 ⁵	<u>b</u> , <u>c</u> , <u>h</u>
	cis-Coen ₂ Cl ₂ ⁺ (298.2)	17	2.4x10 ⁻⁴	0.71x10 ⁵	<u>c</u> , <u>h</u>
	trans-Coen ₂ Cl ₂ ⁺ (298.2)	0.45	3.5x10 ⁻⁵	0.13x10 ⁵	<u>c</u> , <u>h</u>

a Extrapolated from Table 4.2 results.

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TABLE 4.7 A comparison of activation parameters of the spontaneous and of the mercury(II) and thallium(III) catalysed aquations of several chloride complexes

System	$\Delta H^\ddagger /$ kJ mol ⁻¹	$\Delta S^\ddagger /$ JK ⁻¹ mol ⁻¹ (experimental)	$\Delta S^\ddagger /$ JK ⁻¹ mol ⁻¹ (calculated)
ReCl ₆ ²⁻ /Hg ²⁺	123.0±1.7 ^a	+142.3±4.2 ^b	+62.6
ReCl ₆ ²⁻ /Tl ³⁺	115.9±2.9	+104.6±8.4 ^b	+96.6
Co(NH ₃) ₅ Cl ²⁺ spontaneous	93.7	-37.7 ^c	
Co(NH ₃) ₅ Cl ²⁺ /Hg ²⁺	79.1	-67.7 ^d	-62.6
Co(NH ₃) ₅ Cl ²⁺ /Tl ³⁺	79.4±1.3	-15.5±3.8 ^e	-96.6
cis-Coen ₂ (MeNH ₂)Cl ²⁺ /Hg ²⁺	76	-26 ^f	-62.6
cis-Coen ₂ (MeNH ₂)Cl ²⁺ /Tl ³⁺	74±1	-46±3 ^f	-96.6
Cr(NH ₃) ₅ Cl ²⁺ spontaneous	97.9	+37.7 ^c	
Cr(NH ₃) ₅ Cl ²⁺ /Hg ²⁺	62.3±0.8	-56.1±2.9 ^g	-61.9
Rh(NH ₃) ₅ Cl ²⁺ spontaneous	102.1±1.7	-44.8 ^h	
Rh(NH ₃) ₅ Cl ²⁺ /Hg ²⁺	66.9±2.1	-78.7 ^h	-62.9

^a Standard error, determined from Arrhenius programme (Appendix 3e)

^b This work.

^c F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', Wiley, New York, p. 164.

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TABLE 4.8 Relation between second-order rate constants, k_2 , for metal-ion catalysed aquation of ReX_6^{2-} anions and the stability constants, K_1 , for formation of the monohalo- complexes of the metal-ions

	$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} (\text{temp}/\text{K})$	$\log_{10} K_1^a$
<u>ReCl_6^{2-}</u>		
$\text{Hg}^{2+} (\text{aq})$	$4.8 \times 10^{-2} (298.2)$	6.6 to 7.5
$\text{Tl}^{3+} (\text{aq})$	$7.5 \times 10^{-3} (298.2)$	6.2 to 8.1
$\text{Cd}^{2+} (\text{aq})$	$2 \times 10^{-6} (323.2)$	1.2 to 2.5
$\text{In}^{3+} (\text{aq})$	$10^{-6} (323.2)$	1.5 to 2.5
<u>ReBr_6^{2-}</u>		
$\text{Tl}^{3+} (\text{aq})$	780 (300.2)	8.3 to 9.7

a From ref. 15, normally at 298.2K.

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CHAPTER 5

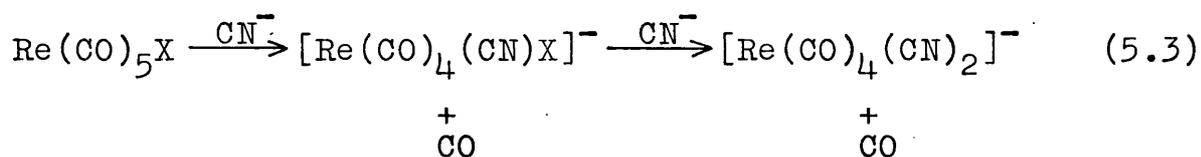
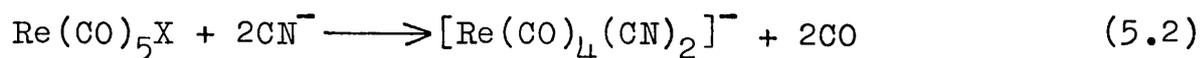
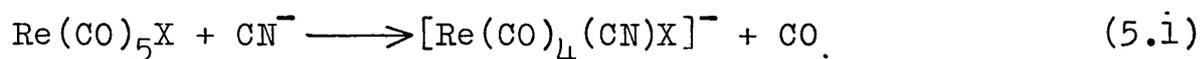
THE KINETICS OF REACTION OF RHENIUM PENTACARBONYL
HALIDES WITH CYANIDE ION IN AQUEOUS METHANOL

CHAPTER 5THE KINETICS OF REACTION OF RHENIUM PENTACARBONYL
HALIDES WITH CYANIDE ION IN AQUEOUS METHANOLINTRODUCTION

There is a lot of chemistry known about the reactions of manganese and rhenium pentacarbonyl halides, and all the chemistry is of substitution reactions. Rhenium(I) and manganese(I) compounds, like those of rhenium(IV) and manganese(IV) (with a d^3 electronic configuration), are especially suitable for kinetic study because of the kinetically inert electronic configuration of the central metal-ion, low-spin d^6 . There is a considerable amount of kinetic data available on the substitution reactions of manganese pentacarbonyl halides,^{1,2} but little on the substitution reactions of rhenium pentacarbonyl halides.

Rhenium pentacarbonyl halides are known to react with an equivalent amount of cyanide ion to produce the rhenium tetracarbonyl cyanide halide anion, $[\text{Re}(\text{CO})_4(\text{CN})\text{X}]^-$ (equation (5.1), where $\text{X} = \text{I}$),³ and with an excess of cyanide ion to produce the rhenium tetracarbonyl dicyanide anion, $[\text{Re}(\text{CO})_4(\text{CN})_2]^-$ (equation (5.2), where $\text{X} = \text{Cl}$).⁴ The kinetics of the reactions of rhenium pentacarbonyl chloride, bromide and iodide with an excess of cyanide ion in aqueous methanolic solution have been investigated and the results are reported herein. Aqueous methanol was the obvious solvent because the rhenium pentacarbonyl halides are all

readily soluble in methanol but not in water, and potassium cyanide is soluble in water, methanol to a smaller extent and little else. Preliminary kinetic runs indicated each of these reactions to follow a kinetic pattern of consecutive first-order reactions. The consecutive first-order reactions sequence was fully substantiated in due course. Both chemical evidence^{3,4} and the kinetic results detailed later suggested that the $[\text{Re}(\text{CO})_4(\text{CN})\text{X}]^-$ anion was the intermediate, rather than $\text{Re}(\text{CO})_5\text{CN}$. The overall reaction monitored was as indicated in equation (5.3).



The presence of excess of cyanide ion did not cause further reaction beyond the formation of the $[\text{Re}(\text{CO})_4(\text{CN})_2]^-$ anion.

The kinetics of reaction of rhenium pentacarbonyl iodide with excess of triphenylphosphine in 70 vol.% methanol-water were followed at 293.2K. This dissociative reaction was used to obtain a rate constant to check against the absence of a dissociative pathway for the first step of the reaction of rhenium pentacarbonyl iodide with excess of cyanide ion. The rate constant obtained was very small and thus supported the observation that the k_{11} (dissociative)

term for the first step of the $\text{Re}(\text{CO})_5\text{I}/\text{CN}^-$ kinetics was so small as to be negligible in comparison with the k_{12} (associative) term.

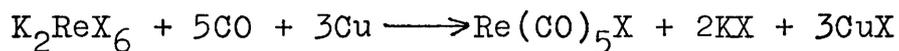
Rate laws, rate constants and activation parameters, where possible, are reported for these reactions, and the mechanisms are discussed. Also of interest is the relationship between the kinetics of the reaction and the Gibbs free energy of transfer, $\delta_m \mu^\ddagger$, of the initial states of $\text{Re}(\text{CO})_5\text{I}$ and CN^- and of the transition state. The data for the Gibbs free energy of transfer of rhenium pentacarbonyl iodide were determined from solubility measurements in the appropriate solvents; the estimation of the Gibbs free energy of transfer of cyanide ion was more approximate due to the lack of published data.

EXPERIMENTAL

Preparation of Reagents

Potassium hexachlororhenate(IV), hexabromorhenate(IV) and hexaiodorhenate(IV) were all prepared by reducing potassium perrhenate solutions with hypophosphorous acid in the appropriate concentrated hydrohalic acid.⁵ The three rhenium pentacarbonyl halides were all prepared by grinding the required amount of precipitated copper powder with the appropriate potassium hexahalorhenate(IV) and then subjecting the mixture to a high pressure of carbon monoxide in a steel bomb reaction vessel at an elevated temperature.⁶ The copper powder was necessary to act as a

halogen acceptor.



For the rhenium pentacarbonyl bromide and iodide preparations, each of the potassium hexahalorhenate(IV)-copper powder mixtures was subjected to an initial pressure of 40 atmospheres of carbon monoxide and the bomb was then kept in an oven at 473K for three days. More extreme conditions were required to obtain a good yield of the rhenium pentacarbonyl chloride, viz. an initial pressure of 70 atmospheres of carbon monoxide and the bomb kept at 523K for three days. All three of the rhenium pentacarbonyl halides were purified by vacuum sublimation between 353 and 373K, the rhenium pentacarbonyl chloride proving the slowest to sublime.

Powder patterns were taken for the three halides using a Philips semi-automatic smoothed D.C. X-ray diffraction generator (operating at 30 kV and 20 mA approximately), a Debye-Scherrer powder camera (of 114.83 mm diameter) and a nickel filter. The powder patterns for all three were very similar. Infra-red spectra were recorded for the three pentacarbonyl halides using a Perkin-Elmer 225 infra-red recording spectrometer. All three had broad bands at 2000 cm^{-1} , presumably due to $\text{C}\equiv\text{O}$ stretching, and also had very similar fingerprint regions. The spectrometer could only scan down to around 200 cm^{-1} and so the band for the Re-X stretching mode was seen only for Re-Cl in $\text{Re}(\text{CO})_5\text{Cl}$ at 295 cm^{-1} . Clark and Crosse⁷ report infra-red bands for the symmetric stretching mode of Re-X (X = Cl, Br, I) in

$\text{Re}(\text{CO})_5\text{X}$ at 294 cm^{-1} , 203 cm^{-1} and 163 cm^{-1} for $\text{Re}(\text{CO})_5\text{Cl}$, $\text{Re}(\text{CO})_5\text{Br}$ and $\text{Re}(\text{CO})_5\text{I}$ respectively.

The ultra-violet—visible spectrum of rhenium pentacarbonyl iodide in methanol agreed with that published by McLean.⁸ The λ_{max} and ϵ_{max} values for rhenium pentacarbonyl iodide, bromide and chloride in 70 vol.% methanol-water and for the iodide in 50 vol.% methanol-water at 298.2K are reported in Table 5.1. Also included in Table 5.1 is the wavelength, λ_{exp} , at which the reaction of each rhenium pentacarbonyl halide with excess of cyanide ion was actually monitored in the various solvent mixtures.

Potassium cyanide, potassium nitrate and triphenylphosphine were AnalaR materials, used as supplied. Potassium perrhenate was prepared from the ammonium perrhenate kindly donated by Professor R. D. Peacock. The methanol solvent was dried over magnesium and iodine previous to redistillation.

Kinetics

All the kinetic runs were monitored spectrophotometrically, the reaction mixtures contained in 1 cm silica cells in the thermostatted cell compartment of a Unicam SP 800 A recording spectrophotometer. The solubilities of $\text{Re}(\text{CO})_5\text{I}$ and $\text{Re}(\text{CO})_5\text{Br}$ in aqueous methanol at 298.2K were also measured with the recording spectrophotometer.

The reaction of rhenium pentacarbonyl halides with excess of cyanide ion exhibited a kinetic pattern

corresponding to two consecutive first-order reactions, the second one being of the order of a hundred times slower than the first. The majority of the kinetic results were obtained for the reaction of the iodide compound with an excess of cyanide ion, for reasons which will be stated later on. The change in optical density with time was monitored at 350 nm, at which wavelength the increase and subsequent decrease of optical density were well marked (Figure 5.1). The isosbestic point for the second stage of the reaction of rhenium pentacarbonyl iodide with excess of cyanide ion in 70 vol.% methanol-water occurs at 301 nm. A few kinetic runs were monitored at this wavelength to gain information solely on the first step, equation (5.1). The same reaction but in 50 vol.% methanol-water was monitored at 350 nm. The reactions of rhenium pentacarbonyl bromide and chloride with an excess of cyanide ion in 70 vol.% methanol-water were monitored spectrophotometrically at 325 and 330 nm respectively. At these wavelengths the changes in absorbance with time for the two reactions were optimum (Figures 5.2 and 5.3).

The final spectra of the reaction mixtures from the $\text{Re}(\text{CO})_5\text{Cl}$, $\text{Re}(\text{CO})_5\text{Br}$ and $\text{Re}(\text{CO})_5\text{I}$ reactions were identical, as one would expect for the generation of a common product, viz. the $[\text{Re}(\text{CO})_4(\text{CN})_2]^-$ anion. The reaction of $\text{Re}(\text{CO})_5\text{I}$ at 323K with triphenylphosphine in 70 vol.% methanol-water was so slow that the reaction flask was thermostatted in a separate water bath. Spectrophotometric observation of aliquots were made at intervals and checks were made regularly to ensure that no solvent loss by evaporation occurred.

FIGURE 5.1

The reaction of rhenium pentacarbonyl iodide
with excess of cyanide ion at 298.2K

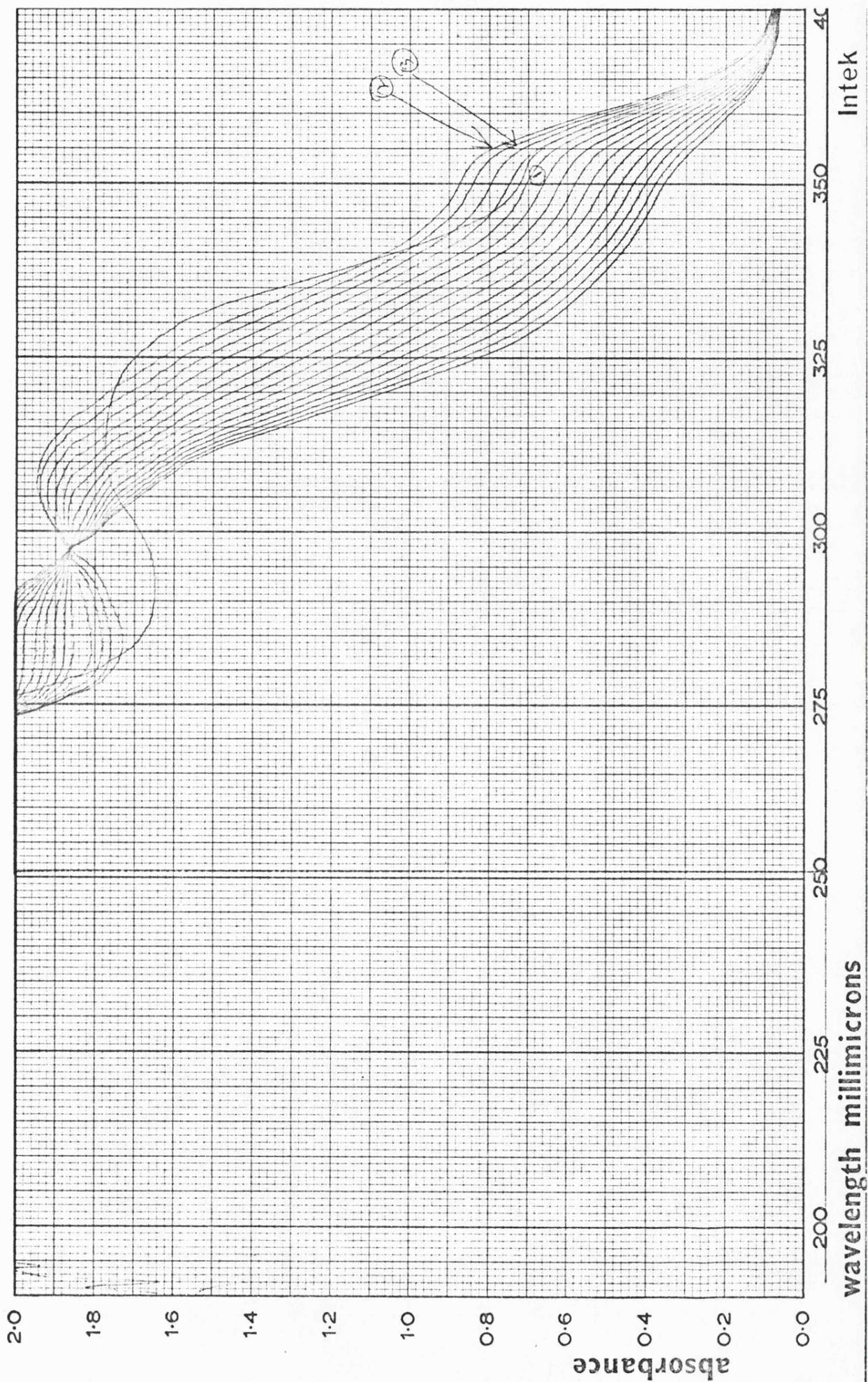


FIGURE 5.2

The reaction of rhenium pentacarbonyl bromide
with excess of cyanide ion at 293.2K

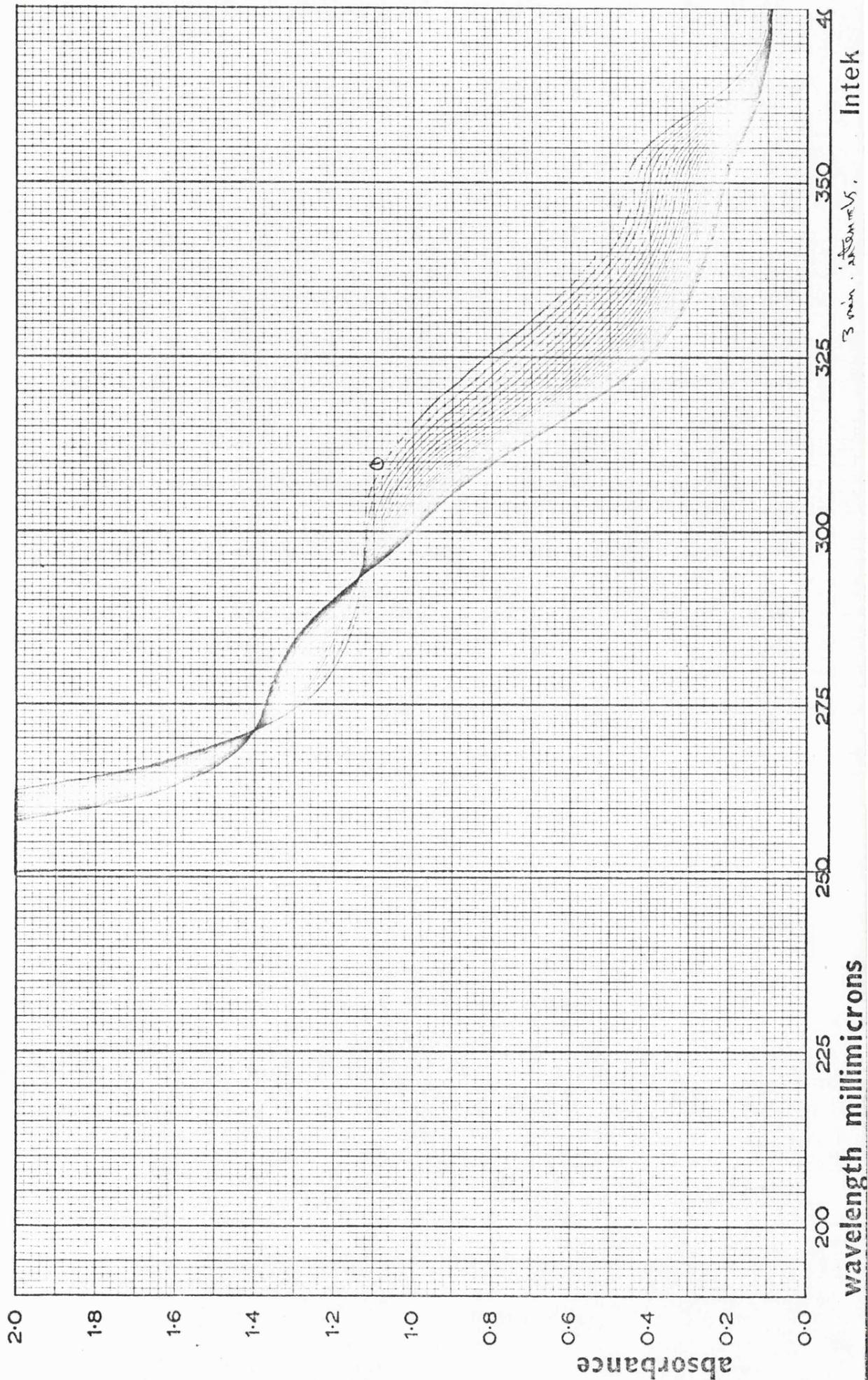
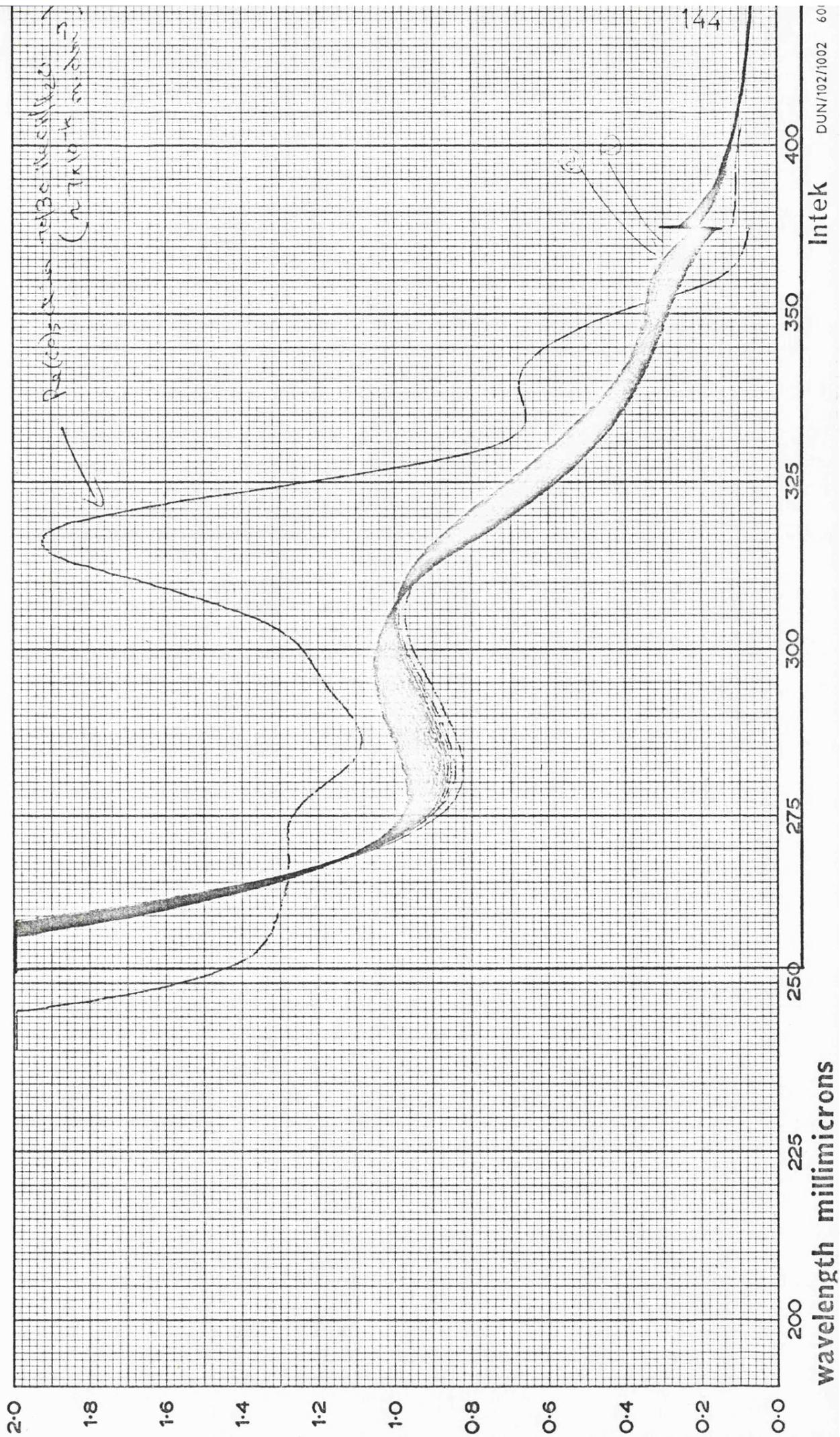


FIGURE 5.3 The reaction of rhenium pentacarbonyl chloride with excess of cyanide ion at 293.2K



The reactions of the rhenium pentacarbonyl halides were conducted in the presence of a large excess of cyanide ion to ensure first-order conditions.[‡] For the two step reaction it was thus possible to analyse the change in optical density with time in terms of two consecutive first-order processes. Values for the respective observed rate constants, $k_{1\text{obs}}$ and $k_{2\text{obs}}$, were determined using a recently published method,¹⁰ suitably modified to deal with the present situation (Appendix 3f).

Treatment of Results

As far as is known, the method used to compute $k_{1\text{obs}}$ and $k_{2\text{obs}}$ for the above consecutive first-order processes is the first application of this method by workers other than those who developed it. The workers who developed the method have used it only once, to compute results for the formation and decay of peroxyxynitrous acid in acidic solutions. The analytical method involved was incorporated as a procedure within a larger computer programme (ALGOL) which could accept rate data in the form of absorbances and times together with the concentration of the starting material for one or more cells. In addition, estimates of the two rate constants, $k_{1\text{obs}}$ and $k_{2\text{obs}}$, and of the molar extinction coefficient, ϵ_B , of the intermediate were required. The known accurate extinction coefficients, ϵ_A and ϵ_C , of the starting material

‡ The dielectric constant is lower for 70 vol.% methanol-water than for aqueous solution, which meant a higher proportion of cyanide was present as HCN rather than as CN^- . It is impossible to estimate the HCN, CN^- ratio in the solvent mixture since the requisite thermodynamic parameters are not available. However, the total concentration of cyanide in each run was high and this suppressed the concentration of HCN to less than 1.5% of the total cyanide.⁹

and final product at the same wavelength were also necessary.

Briefly, the method uses the difference between observed and calculated dependence of absorbance on time to correct the estimated rate constants and extinction coefficient, thus producing improved values. The latter are used again, the new calculated dependence of absorbance on time being compared to the observed dependence, to obtain a new set of improved values. This cycle continues until the values converge, i.e. the rate constants, k_{1obs} and k_{2obs} , and the extinction coefficient, ϵ_B , do not alter significantly between cycles. The calculations are tedious but trivial in the sense of computer techniques, the most time consuming step being the inversion of a 3×3 matrix.

In the reaction of rhenium pentacarbonyl halides with an excess of cyanide ion in aqueous methanol (at a wavelength where the increase and subsequent decrease in absorbance were optimum), the absorbance increased rapidly before decreasing relatively slowly (Figures 5.1, 5.2 and 5.3). It proved important as far as the analysis was concerned to have sufficient experimental points on the first part of the curve (before the maximum) to define this part of the dependence of the absorbance on time. Otherwise the analysis did not converge satisfactorily, the calculation seemingly treating these points as a scatter about a single decay curve. It was similarly important to have ample points for the second stage (beyond the maximum of the reaction curve) in order that an accurate value of k_{2obs} could be computed. Further, it proved important to provide reasonable initial estimates of the rate constants and the extinction coefficient of the intermediate. A poor

estimate of the initial value for these parameters sometimes made it necessary for the computer to make a large calculated correction to the initial value after the first cycle. Such a large correction often resulted in a negative rate constant. A loop in the programme would then halt the analysis, otherwise the system encountered some arithmetic stumbling block leading to difficulties with, for example, the matrix inversion. A poor initial estimate also often required that the analysis proceeded through many cycles, the programme allowing up to 50. However, with experience and as one's judgement improved, the number of cycles required was rarely more than 5.

The very nature of the analysis means, however, that the data for both stages, rapid rise and slower drop in absorbance, must be of comparable quality. It is not possible, for example, to calculate a precise value for $k_{2\text{obs}}$ together with an approximate estimate of $k_{1\text{obs}}$. The overall reaction was speeded up so much by operating in 50 vol.% methanol-water (instead of 70 vol.%), by raising the temperature above 308K, by using high concentrations of cyanide, by using $\text{Re}(\text{CO})_5\text{Cl}$ or $\text{Re}(\text{CO})_5\text{Br}$ rather than $\text{Re}(\text{CO})_5\text{I}$ or by any combination of two or more of these four situations, that it became impossible to compute values of $k_{1\text{obs}}$ and $k_{2\text{obs}}$. In such cases, very few points for the first step, equation (5.1), were obtained, while the second step, equation (5.2), followed at a reasonable rate. Conversely, the overall reaction was slowed down so much by operating below 293K, by using 70 vol.% methanol-water as the solvent, by operating with low concentrations of cyanide, by working with $\text{Re}(\text{CO})_5\text{I}$ rather than $\text{Re}(\text{CO})_5\text{Cl}$ or $\text{Re}(\text{CO})_5\text{Br}$, or again by any

combination of two or more of these four situations, that values of k_{1obs} and k_{2obs} could not be computed. In this case the first step yielded ample points for the analysis but the second step was so slow that one was never sure of it reaching completion.

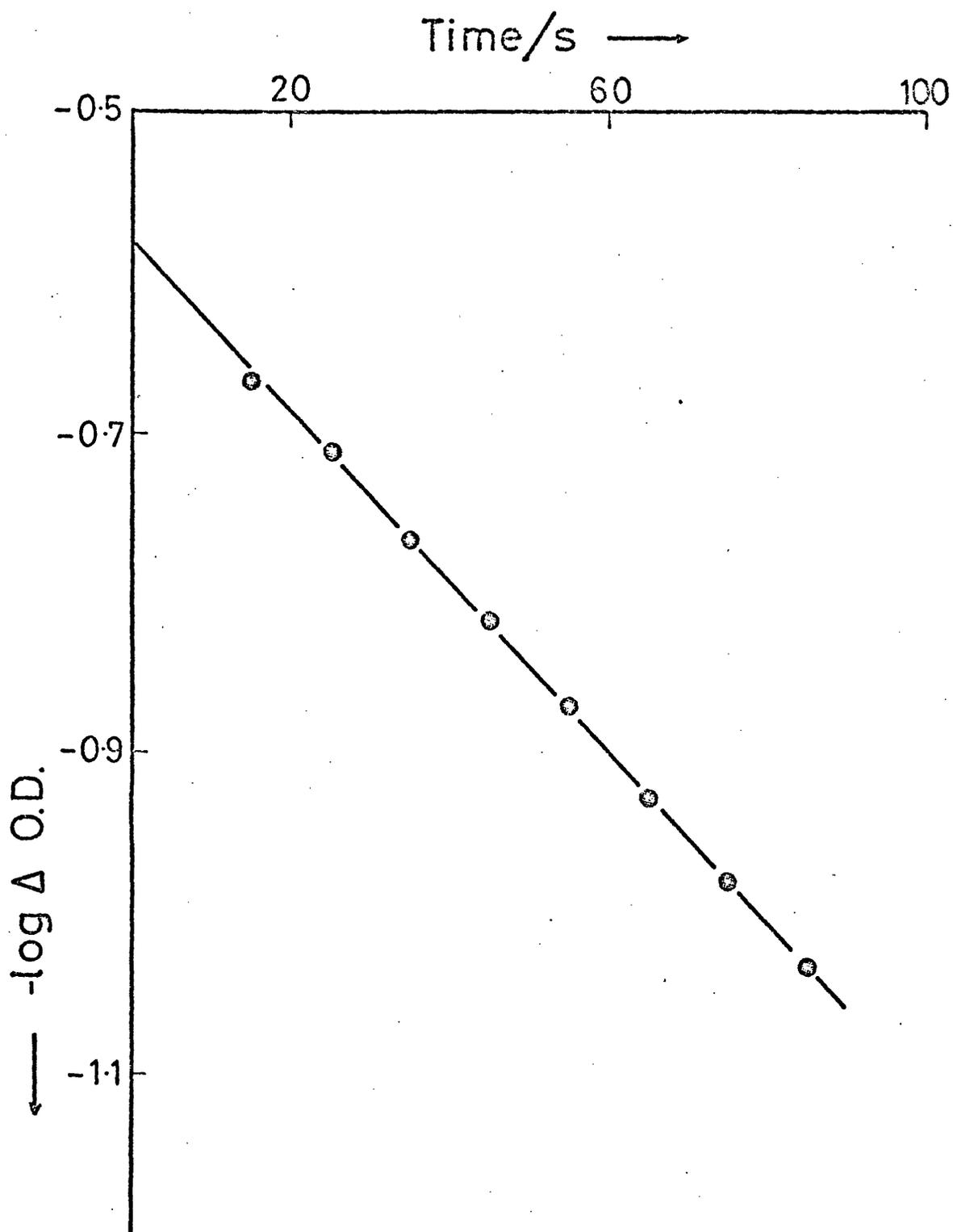
When either of these two extreme situations occurred, the calculations of k_{1obs} and k_{2obs} were so dependent upon one another that insufficient or incomplete observed data for one first-order reaction made it impossible to obtain rate constants for either of the consecutive first-order reactions. At this point a loop in the programme would halt the analysis. Consequently, the only reactions that yielded accurate values for k_{1obs} , k_{2obs} and ϵ_{max} were those that were slow enough to observe a reasonable number of points for the first step but fast enough to push the second step to completion within 24 hours. The kinetic runs were thus restricted to a small temperature range and the majority of results are for the reaction of rhenium pentacarbonyl iodide in 70 vol.% methanol-water. Due to the faster reactions of rhenium pentacarbonyl chloride and bromide, the only results obtained for these two compounds were at 293.2K (and 288.2K for the latter) in 70 vol.% methanol-water.

In summary, the method proposed by Moore and co-workers is found to be valuable and one worthy of wider usage. The general availability of computer routines for matrix inversion and related problems removes the major arithmetical hurdle and has the advantage, as Moore points out, of leading to a satisfactory statistical analysis of the errors on the calculated parameters.

In any one run, the time delay between mixing the thermostatted reactants and obtaining the first point on the curve for the first step ranged between 13 and 18 seconds. As mentioned earlier, the computer analysis requires the accurate values of ϵ_A and ϵ_C , where ϵ_A is the molar extinction coefficient of the rhenium pentacarbonyl halide and ϵ_C is the molar extinction coefficient of the final product, both measured at the monitored wavelength, λ_{exp} .

Initially, one might have thought that ϵ_A could be determined by measuring the optical density of a no-cyanide blank, viz. a solution containing the usual concentration of rhenium pentacarbonyl halide with solvent added instead of the cyanide solution. However, this method makes no allowance for any absorbance by the cyanide solution or for any pipetting errors. Hence, the idea of using a blank to measure ϵ_A was ruled out. What was required was some function of the optical density that could be extrapolated backwards to time zero with more confidence than the optical density-time curves themselves. For a one step first-order reaction a plot of log of the optical density against time is linear, and so the early stages of the first step of a consecutive two first-order step reaction should closely resemble a simple first-order reaction. Thus the obvious plot to try was $\log \Delta O.D.$ against time, where $\Delta O.D.$ is the difference between the maximum optical density observed and the optical density at each point. The plot proved linear up to at least four half-lives. Beyond four half-lives, the contribution from the second step was no longer negligible and the linearity of the log plot was destroyed. Such plots were made for every cyanide concentration of each run and

FIGURE 5.4 Plot of $\text{Log } \Delta\text{O.D.}$ against time for the first step of the reaction of rhenium pentacarbonyl iodide with excess of cyanide ion at 298.2K



the resulting straight lines were extrapolated back to time zero to give $\Delta O.D._0$, where $\Delta O.D._0$ is the difference between the observed optical density maximum and the optical density of the mixed reactants at time zero. (Figure 5.4)

Once the $O.D._0$ value had been determined, ϵ_A was calculated from Beer's Law,¹¹

$$\epsilon_A = \frac{O.D._0}{A_0 d} ,$$

where $d = 1$ cm and $A_0 =$ initial concentration of $Re(CO)_5X$ in the cell. Once the ϵ_A value was known, the ϵ_C value was calculated by the relationship,

$$\frac{O.D._0}{O.D._\infty} = \frac{\epsilon_A}{\epsilon_C} ,$$

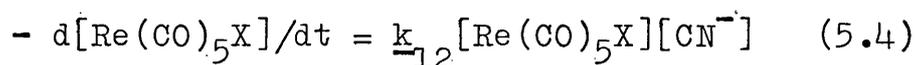
where $O.D._\infty$ is the optical density of the product solution after infinite time, i.e. 24 hours or more. Approximate values of k_{1obs} and k_{2obs} were estimated from the following equation,¹²

$$k_{obs} = \frac{\ln 2}{\tau_{1/2}} ,$$

where $\tau_{1/2}$ is the half-life of any one step. Such estimates, based on the assumption that the first step had gone to completion and the second step began at the absorbance curve maximum, were good enough for the computer analysis. The same equation was used to estimate the rate constant for the reaction of rhenium pentacarbonyl iodide with triphenylphosphine in 70 vol.% methanol-water at 323.2K.

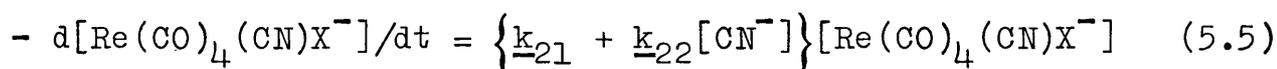
RESULTS

Computed first-order rate constants, k_{obs} , for the reaction of rhenium pentacarbonyl halides with cyanide ion are reported in Table 5.2. For the first step of the reaction of all three halides, plots of $k_{1\text{obs}}$ against cyanide concentration are linear with the best straight line passing through the origin. The intercept of the least-mean-squares computed straight line on the $k_{1\text{obs}}$ axis is within its 90% confidence limits of zero (Appendix 3d). The rate law needed to account for this result is shown in equation (5.4);



(X = Cl, Br, I)

For the slower second step, plots of $k_{2\text{obs}}$ against cyanide concentration are again linear. However, the plot has a significant intercept this time, indicative of some dissociative character contribution to the reaction. The rate law needed to accommodate this observation is of the type shown in equation (5.5);



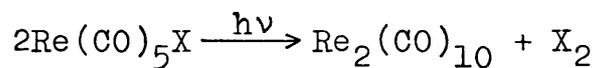
(X = Cl, Br, I)

Indeed, the k_{21} term for the reactions of the rhenium pentacarbonyl chloride and bromide is much more important than the $k_{22}[\text{CN}^-]$ term of the rate law.

Activation parameters were computed using a least-mean-squares programme (Appendix 3e), from the variation in temperature of the rate constants, k_{12} , k_{21} and k_{22} , for the

reaction of rhenium pentacarbonyl iodide with an excess of cyanide ion in 70 vol.% methanol-water. The activation parameters for the first step were computed from each individual $\underline{k}_{1\text{obs}}/[\text{CN}^-]$ quotient. Activation parameters for the second step were computed from the variation of the \underline{k}_{21} and \underline{k}_{22} values themselves with temperature. The \underline{k}_{21} and \underline{k}_{22} values were previously determined from plots of $\underline{k}_{2\text{obs}}$ against cyanide concentration using a least-mean-squares straight line programme (Appendix 3d). The activation parameters thus determined, with an indication of their uncertainties, are reported in Table 5.3.

The solubilities of rhenium pentacarbonyl iodide and rhenium pentacarbonyl bromide in the appropriate solvent mixtures were determined by spectrophotometric measurement and are reported in Table 5.4. The solutions used for this purpose were well thermostatted and saturated to ensure equilibration. Care was taken not to expose the reaction flasks to light because of the photolysis that would then occur to produce dirhenium decacarbonyl and halogen, i.e.



The rhenium pentacarbonyl iodide solutions were particularly susceptible to photolysis and a characteristic yellow iodine colour was observed with uncovered reaction flasks within 24 hours.

DISCUSSIONReaction Sequence

Hieber et al.⁴ maintained that the intermediate formed upon the attack of cyanide ion on $\text{Re}(\text{CO})_5\text{I}$ is the cis- $[\text{Re}(\text{CO})_4(\text{CN})\text{I}]^-$ anion rather than $\text{Re}(\text{CO})_5\text{CN}$. This is reasonable when one considers the bonding involved in the octahedral $\text{Re}(\text{CO})_5\text{I}$. Carbonyl ligands back-bond strongly with central metal-ions that have plenty of electron density in π non-bonding orbitals. In $\text{Re}(\text{CO})_5\text{I}$, the carbonyl ligand opposite the iodide ligand has little or no competition from the iodide for back-bonding with rhenium(I). Hence, the Re-CO bond opposite the Re-I bond is the strongest of all the Re-CO bonds. Consequently, the first ligand to be substituted for cyanide is one of the carbonyl ligands cis to the iodide ligand.

If $\text{Re}(\text{CO})_5\text{CN}$ were the intermediate rather than the $[\text{Re}(\text{CO})_4(\text{CN})\text{I}]^-$ anion, it would be common to the reaction of all three rhenium pentacarbonyl halides with excess of cyanide ion. This would mean that the rate constants for the second step would be identical for all three rhenium pentacarbonyl halides. The results in Table 5.2 clearly invalidate this idea, since none of the second step rate constants agree for the reaction of the three compounds with excess of cyanide ion.

It is possible to imagine the CN^- nucleophile attacking one of the carbonyl carbon atoms as in the cases of, for example, the attack of N_3^- , NCO^- , NH_2OH at $\text{M}(\text{CO})_6$ where

M = Cr, Mo, W,¹³ the attack of primary and secondary amines at $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{L}]^+$,¹⁴ and the base-catalysed nucleophilic attack of primary aliphatic amines upon cationic metal carbonyl complexes of manganese and rhenium.¹⁵ Moreover, Gillard¹⁶ claims that HCN attacks at the 2-position of co-ordinated ligands in iron(II) complexes of the $\text{Fe}(\text{bipy})_3^{2+}$ type, to form quaternised heterocycles. However, Hieber⁴ has established the formation of the $[\text{Re}(\text{CO})_4(\text{CN})_2]^-$ product and has further support to this effect from Behrens and co-workers.³

Rate Laws

The rate laws obtained, equations (5.4) and (5.5), suggest that the first step of the overall reaction of each of the three rhenium pentacarbonyl halides with cyanide ion is bimolecular. The mechanism presumably involves associative attack of the incoming cyanide ion at the central rhenium(I) cation, despite the high electron density in the t_{2g} orbitals which the incoming cyanide ion must penetrate. On the other hand, the second step of the overall reaction, when the anion is $[\text{Re}(\text{CO})_4(\text{CN})\text{Cl}]^-$ or $[\text{Re}(\text{CO})_4(\text{CN})\text{Br}]^-$, appears to proceed by a predominantly dissociative mechanism. The reaction of the $[\text{Re}(\text{CO})_4(\text{CN})\text{I}]^-$ anion with cyanide ion is less straightforward and seems to proceed via parallel associative and dissociative pathways ($k_{21} \sim k_{22}[\text{CN}^-]$). The trend from associative attack for the first step to a more dissociative second step parallels the pattern observed for the step-wise reaction of the iron(II) complex of the hexadentate Schiff base ligand NN^{III} -bis-(2-pyridyl-methylene)-triethylenetetramine with cyanide ion.¹⁷

One can make a comparison between rhenium(I) and iron(II) compounds when both are low-spin, i.e. a t_{2g}^6 electronic configuration. The first step of the cyanide ion attack is associative, but the second step of the cyanide ion attack is a dissociative process. The third step of the cyanide ion attack is so slow that a rate constant is unobtainable. The authors explain the trend from associative to dissociative character by proposing that as more cyanide ions replace the organic ligands the electron density builds up on the iron cation. The central iron cation already has a t_{2g}^6 electronic configuration and further increases in electron density make it more difficult for further cyanide nucleophiles to attack via an associative mechanism.

Rhenium pentacarbonyl iodide is the least polar of the three halides discussed here and this is reflected by its higher volatility. The electron density on the rhenium atom is higher in rhenium pentacarbonyl iodide than in the more polar bromide and chloride analogues. The attack of the first cyanide nucleophile at all three rhenium pentacarbonyl halides is purely associative. However, the central rhenium cation in the $[\text{Re}(\text{CO})_4(\text{CN})\text{I}]^-$ anion now has even more electron density pushed on to it and the electron density has now reached such a level that the complex anion cannot cope with a purely associative attack by a second cyanide nucleophile. Hence, part of the second step perforce has to proceed via a dissociative pathway.

One may use the same argument to explain the kinetics of the reactions of each of the $[\text{Re}(\text{CO})_4(\text{CN})\text{Br}]^-$ and

$[\text{Re}(\text{CO})_4(\text{CN})\text{Cl}]^-$ anions with cyanide ion. The even greater dissociative character for these reactions is possibly because of the greater polarity of the Re-Br and Re-Cl bonds (compared to the Re-I bond) in the $[\text{Re}(\text{CO})_4(\text{CN})\text{X}]^-$ anion.

Kinetic Parameters

The activation entropies (Table 5.3) for the two steps of the reaction of rhenium pentacarbonyl iodide with cyanide ion are not inconsistent with the interpretation of the proposed rate laws, if one assumes that solvation and solvation changes play a dominant rôle in determining these activation entropies. The bimolecular reaction between the two negatively charged species, $[\text{Re}(\text{CO})_4(\text{CN})\text{I}]^-$ and CN^- , would be expected to have a larger negative entropy of activation than the bimolecular reaction between the neutral and the negatively charged species, $\text{Re}(\text{CO})_5\text{I}$ and CN^- . The simple electrostatic model,¹⁸ for estimating the activation entropy for a reaction between ions in solution, suggests that the former bimolecular reaction might be expected to have an activation entropy of $-16 \text{ J K}^{-1} \text{ mol}^{-1}$ (atomic radii of $\text{C}\equiv$ and $\text{O}\equiv$ are 0.602\AA and 0.50\AA respectively;¹⁹ atomic radius of rhenium is 1.373\AA ²⁰ and the radius of Re^{4+} is 0.63\AA ²¹ and so a guess for the radius of Re^+ would be about 1.2\AA ; the radius of CN^- is 1.82\AA ²²). The dissociative pathway (k_{21}) of the reaction of the $[\text{Re}(\text{CO})_4(\text{CN})\text{I}]^-$ anion with cyanide ion has an unusually large negative entropy of activation. Presumably, this may be due partly to solvation changes attendant upon changes in charge and dipole distribution upon formation of the transition state.

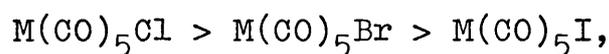
To verify the dissociative contribution to the second step of the overall reaction, several attempts were made to prepare $\text{Na}[\text{Re}(\text{CO})_4(\text{CN})\text{I}]$, the sodium salt of the intermediate anion. Two attempts were made, using THF as solvent, following the preparation mentioned in a paper by Behrens et al.,³ but a black oily product was the result. Behrens et al.³ prepared the same salt by refluxing rhenium pentacarbonyl iodide and sodium bis(trimethylsilylamide) in benzene for one hour. Hence, a third attempt at preparing the sodium salt was made by refluxing rhenium pentacarbonyl iodide and sodium cyanide in sodium-dried benzene for one hour. Pale yellow crystals were isolated, washed with petrol and dried in a vacuum desiccator over phosphorus pentoxide.

It was hoped to observe the kinetics of reaction of the salt with excess of cyanide ion and with excess of triphenylphosphine at 298.2K in 70 vol.% methanol-water, to verify that part of the reaction goes via a mechanism independent of the nature and concentration of the incoming nucleophile. However, very little reaction with excess of cyanide was observed. The ultra-violet spectra of the sodium salt in solution and of the final solution of the consecutive reaction were very similar. In addition, an infra-red spectrum of the salt did not show the $\text{C}\equiv\text{N}$ stretching mode band at 2150 cm^{-1} reported by Behrens. It is probable that the pale yellow crystals were the sodium salt of the $[\text{Re}(\text{CO})_4(\text{CN})_2]^-$ anion, i.e. the preparation had gone right through to the dicyano product and so a check on the dissociative pathway for the second step was curtailed.

The relatively large uncertainties in the activation parameters are a consequence of the short temperature range to which the reaction was restricted. In view of this, any attempt to extend a detailed interpretation of these activation entropies would seem unwise. However, one might note that the activation enthalpies for the attack of cyanide ion at both $\text{Re}(\text{CO})_5\text{I}$ and $[\text{Re}(\text{CO})_4(\text{CN})\text{I}]^-$ are low, considering that rhenium(I) has a t_{2g}^6 electronic configuration, and thus, in the approximately octahedral environment of the $\text{Re}(\text{CO})_5\text{I}$ and $[\text{Re}(\text{CO})_4(\text{CN})\text{I}]^-$ species, it should have high ligand field stabilisation and high activation energies.

Reactivities

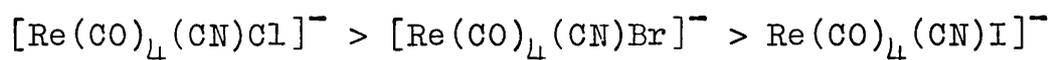
The relative reactivities of the series of compounds $\text{M}(\text{CO})_5\text{X}$, where $\text{M} = \text{Mn}$ or Re and $\text{X} = \text{Cl}$, Br or I , towards substitution, follow the order



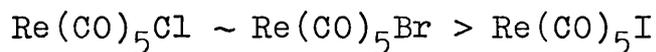
which is also the order of relative polarities and volatilities. Such an order has been established, for example, for the reactions of $\text{Mn}(\text{CO})_5\text{X}$ ^{23,24} and of $\text{Re}(\text{CO})_5\text{X}$ ²⁴ with triphenylphosphine and for carbon monoxide exchange at $\text{Re}(\text{CO})_5\text{X}$.²⁵ It is unfortunate that these are the only close reactions available for comparison with the present $\text{Re}(\text{CO})_5\text{X}/\text{CN}^-$ reaction, because the above reactivity trend has only been established for reactions that proceed via a dissociative mechanism. Moreover, these comparable reactions were carried out in very different solvents from aqueous methanol, viz. toluene, xylene, chloroform, carbon tetrachloride and n-octane. One can compare the reaction of triphenylphosphine

with rhenium pentacarbonyl iodide in 70 vol.% methanol-water and in n-octane.²⁴ The observed rate constants, k_{obs} , are approximately 3×10^{-6} and $3 \times 10^{-4} \text{ s}^{-1}$ for aqueous methanol and n-octane solvents respectively, although at different temperatures (323 and 353K respectively). Another comparison can be made between the reaction of rhenium pentacarbonyl iodide with triphenylphosphine in 70 vol.% methanol-water and the isotopic exchange reaction of carbon monoxide with rhenium pentacarbonyl iodide in toluene²⁵, both at 323K. The k_{obs} values are approximately $3 \times 10^{-6} \text{ s}^{-1}$ for the former reaction and $2 \times 10^{-6} \text{ s}^{-1}$ for the latter.

Despite the difference in solvents, the order of reactivity for the dissociative pathway of the reaction between the $[\text{Re}(\text{CO})_4(\text{CN})\text{X}]^-$ anion and CN^- in 70 vol.% methanol-water is analogous to the reactivity trend mentioned above (Table 5.2).



The associative attack of cyanide ion at $\text{Re}(\text{CO})_5\text{X}$ for the first step of the overall reaction has a similar trend in reactivity:



As can be seen from Table 5.2, the associative contribution to the reaction of the $[\text{Re}(\text{CO})_4(\text{CN})\text{X}]^-$ anion with cyanide ion (when X = Cl or Br) is so small that it might be considered negligible. Therefore, one cannot confidently assign an order of reactivity to the three

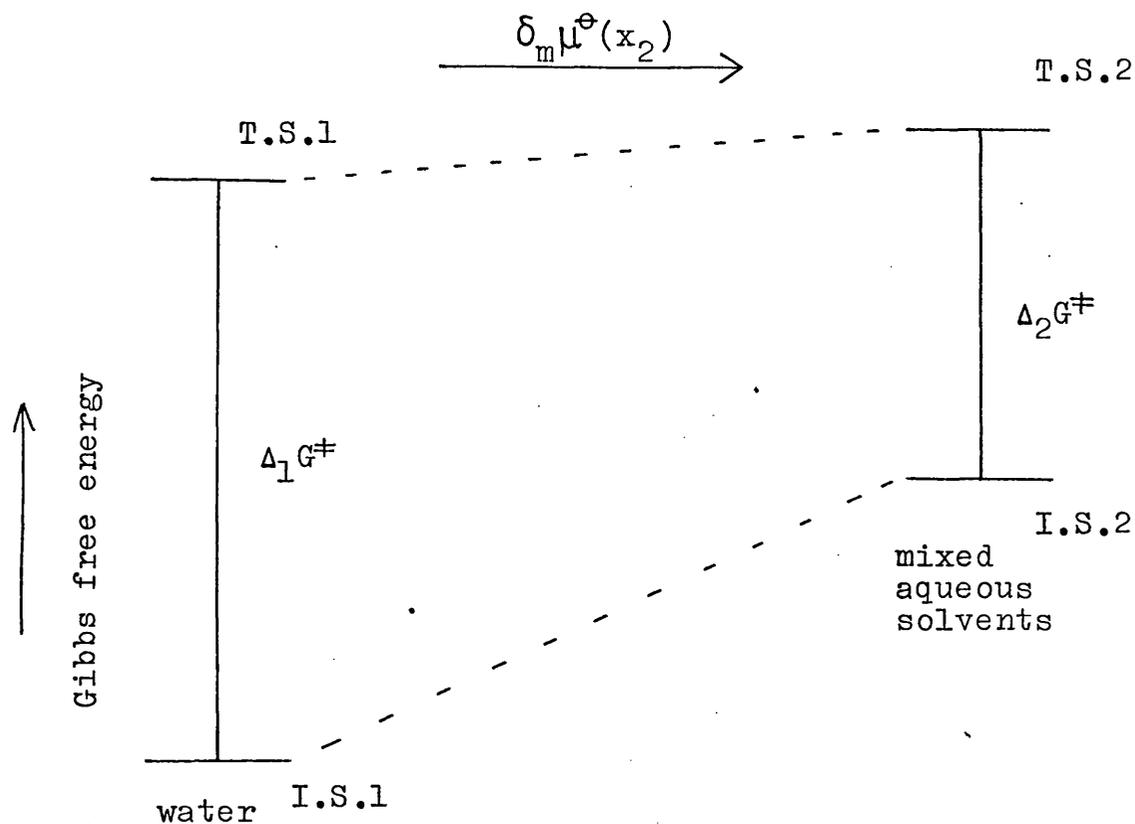
rhodium pentacarbonyl halides for this pathway of the second step.

Relationship between Reactivities and Transfer Parameters

Much work has already been done on the bimolecular reactions between low-spin iron(II) complexes with cyanide ion in a series of aqueous organic binary solvent mixtures; for example, $\text{Fe}(\text{phen})_3^{2+}$ with cyanide ion²⁶ and $\text{Fe}(\text{SB})_3^{2+}$ with cyanide ion,²⁷ where SB is the Schiff base ligand α -(2-pyridyl)benzylideneaniline. The results show that the rate of the bimolecular reaction markedly increases as the proportion of non-aqueous component of the solvent mixture increases. The reason for this effect is only now emerging from some work done by Burgess et al.²⁸ on the reaction of $\text{Fe}(\text{bipy})_3^{2+}$ with cyanide ion in a variety of aqueous mixtures.

The effect appears to be controlled by relative changes in the initial states of the cyanide ion upon transfer to a solvent mixture richer in the organic component. When comparing the bimolecular reaction in two solvent mixtures (between which the transfer occurs), the initial states of the iron(II) complex are both big. Hence, the transfer parameter, $\delta_m \mu^\ominus$, between the two initial states for the iron(II) complex, on transfer from aqueous to mixed aqueous solvents, is relatively small. However, the initial states for the cyanide ion are small and there is likely to be a big solvation change on transfer from one initial state of the cyanide ion to the other initial state. The cyanide ion is less favourably solvated in mixed aqueous solvents than in water and this is reflected by its higher chemical potential,

i.e. a relatively large, positive $\delta_m \mu^\ominus$ (see diagram below). This limitation on the solubility of potassium cyanide was the major reason for using methanol-water solvent mixtures, as mentioned previously.



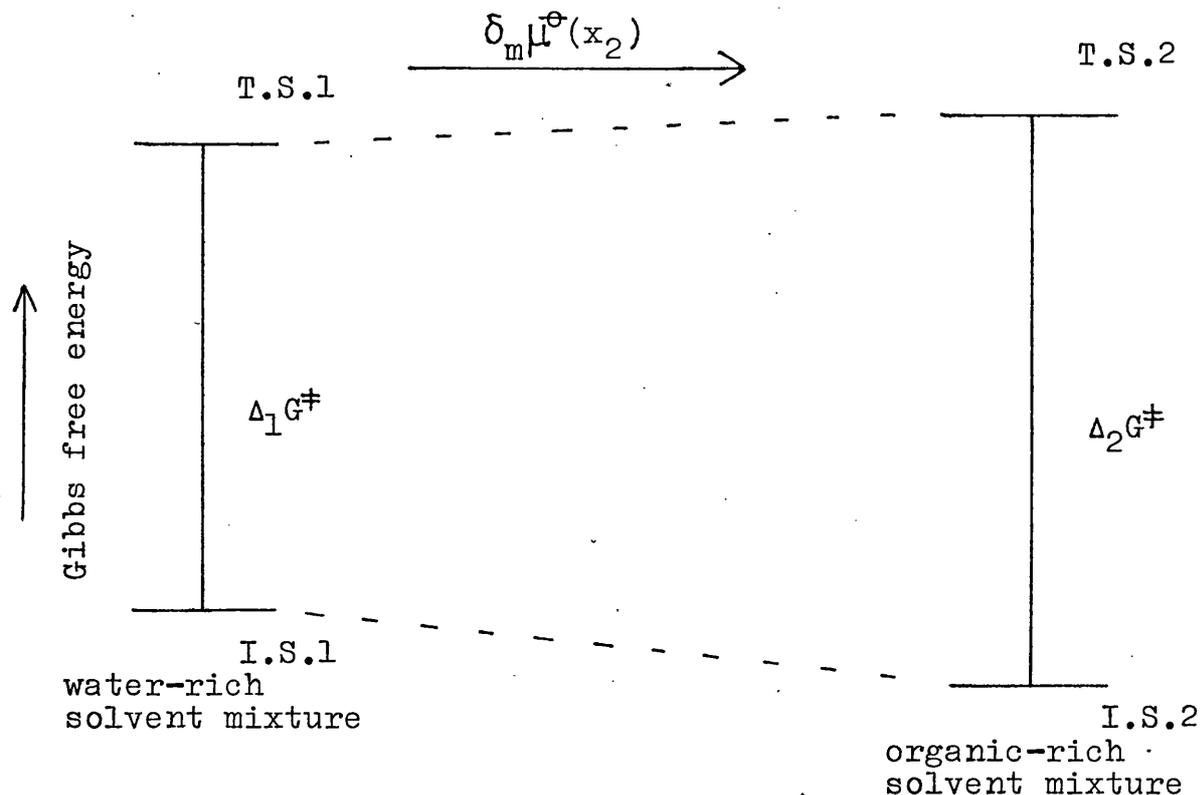
The large change in ΔG^\ddagger , on transfer to a solvent mixture with a large organic component, appears to be due mainly to the change in solvation around the relatively small cyanide ion in the initial state.

Burgess et al. show that $\delta_m \mu^\ominus(\text{CN}^-)$ is indeed dominant because the ratio of $k_2[\text{CN}^-]$ in aqueous and in mixed aqueous solvents observed is similar to the $k_2[\text{CN}^-]$ ratio predicted from $\delta_m \mu^\ominus(\text{CN}^-)$, considering only the transfer between the initial states of the cyanide ion and assuming $\delta_m \mu^\ominus(\text{Fe}^{\text{II}})$

complex, initial state) and $\delta_m \mu^\ominus$ (transition state) are both zero. The authors have some evidence for assuming that $\delta_m \mu^\ominus$ (Fe^{II} complex, initial state) = zero is a good approximation. The evidence is that the rate of dissociative aquation of the iron(II) complex varies little with solvent composition, which would stem from little change in ΔG^\ddagger (the change in Gibbs free energy between the initial and the transition states) upon the transfer between solvents.

The reaction of rhenium pentacarbonyl iodide with cyanide ion goes more slowly in 70 vol.% methanol-water than in 50 vol.% methanol-water (Table 5.2). In the light of the aforementioned work on Fe(bipy)₃²⁺/CN⁻ system, this result is somewhat surprising. The same changes obviously occur on transfer of the cyanide ion in its initial state as discussed above. To account for the drop in reaction rate, as the proportion of organic component in the solvent mixture increases, one must assume that the change in the initial states of the rhenium pentacarbonyl iodide upon transfer is even greater than, and of opposite sign to, that of the cyanide ion.

The idea of a difference in sign for $\delta_m \mu^\ominus$ [Re(CO)₅I] compared to $\delta_m \mu^\ominus$ (CN⁻) is qualitatively reasonable, since the solubility of Re(CO)₅I is greater in methanol than in water. This results in a negative value for $\delta_m \mu^\ominus$ upon transfer from a lesser to a greater organic-rich aqueous solvent mixture (see diagram below).



As a result, ΔG^\ddagger increases upon increase in the proportion of organic component of the solvent mixture, and this is governed by the change in solvation around the rhenium pentacarbonyl iodide.

The drop in reaction rate upon transfer to the more organic-rich solvent mixture suggests that the Gibbs free energy of transfer of $\text{Re}(\text{CO})_5\text{I}$, $\delta_m \mu^\ominus[\text{Re}(\text{CO})_5\text{I}]$, dominates the overall change in Gibbs free energy, rather than CN^- , i.e. the favourable effect on the solvation of rhenium pentacarbonyl iodide, upon increase in the proportion of the organic component of the solvent mixture, is probably greater in magnitude than the unfavourable effect on the solvation of the cyanide ion.

One would like to test quantitatively the supposition that $\delta_m \mu^\ominus[\text{Re}(\text{CO})_5\text{I}]$ is larger in magnitude than $\delta_m \mu^\ominus(\text{CN}^-)$ for

the transfer from 50 vol.% to 70 vol.% methanol-water mixtures. Unfortunately, the lack of quantitative thermochemical information on the cyanide ion in solution prevents an unequivocal verification of this supposition. However, the general approach one might use can still be outlined (next paragraph).

From the solubilities at 293.2K reported in Table 5.4, the Gibbs free energy of transfer of $\text{Re}(\text{CO})_5\text{I}$, $\delta_m \mu^\ominus[\text{Re}(\text{CO})_5\text{I}]$, can be estimated from the following relationship,

$$\delta_m \mu^\ominus[\text{Re}(\text{CO})_5\text{I}] = -RT \ln (S_{\text{II}}/S_{\text{I}}),$$

for the transfer of $\text{Re}(\text{CO})_5\text{I}$ from solvent I (50 vol.% methanol-water) to solvent II (70 vol.% methanol-water), where S is the solubility. Thence, assuming activity coefficients of unity (which will be approximately correct because these solutions are dilute and the solute is uncharged), $\delta_m \mu^\ominus[\text{Re}(\text{CO})_5\text{I}] = -3.3 \text{ kJ mol}^{-1}$ at 293.2K.

The process of estimating a value for $\delta_m \mu^\ominus(\text{CN}^-)$, for the transfer between the same two solvent mixtures already mentioned, is far less simple and satisfactory. Since there are no quantitative thermochemical data on cyanide ion, one must assume that it is equivalent to chloride ion. This assumption is based upon the close similarity of ionic radii, 1.82\AA^{22} for cyanide ion and 1.81\AA^{21} for chloride ion, and of single-ion hydration enthalpies, -347 kJ mol^{-1} ²⁹ for cyanide ion and -351 kJ mol^{-1} ²⁹ for chloride ion. (The single-ion hydration enthalpies are based on the simple assumption that $\Delta H_{\text{si}}\text{Cs}^+(\text{g}) = \Delta H_{\text{si}}\text{I}^-(\text{g})$, which differs from the assumption used for the single-ion split in Chapter 3.) Support for

the assumption that cyanide ion is thermochemically equivalent to chloride ion arises from its success as a basis for similar estimates and discussions relating to the reaction of the $\text{Fe}(\text{bipy})_3^{2+}$ cation with cyanide ion in aqueous methanol and in aqueous t-butyl alcohol.²⁸ Even the use of this assumption is far from straightforward because there are many sources available for the estimation of $\delta_m \mu^\ominus(\text{Cl}^-)$ values in aqueous methanol mixtures, and no two sources agree on the values.

The three main sources are Wells,³⁰ de Ligny and Alfenaar³¹ and Feakins et al.³². Wells bases his estimates on a modified Born expression for a tetrahedral aquated proton and only deals with solvent compositions up to 50 wt.% methanol. De Ligny and Alfenaar use a modified Born expression for their estimates (but a different expression from Wells), in which they consider the transfer comprising of two contributions, an electrical and a neutral contribution. The authors only give estimates of $\delta_m \mu^\ominus(\text{Cl}^-)$ for two solvent compositions. Feakins et al. calculated their estimates from an over-simplified Halliwell and Nyburg³³ method of deriving single-ion values, based on the dependence of ΔG_t^\ominus for the hydrogen halides, HX, on $1/r_a$, and on the dependence of ΔG_t^\ominus for a salt, MCl, on $1/r_c$, where r_a and r_c are the crystallographic radii of anions and cations respectively. Feakins et al. subsequently expressed doubts on their method for deriving single-ion values.³⁴

It was impossible to obtain satisfactory values of $\delta_m \mu^\ominus(\text{Cl}^-)$ from these sources because some of the sources lacked values for the appropriate solvent mixtures, the

assumptions used to make the single-ion split were unreasonable and the values quoted in the different sources for the same solvent mixtures were inconsistent. The possibility of obtaining values of $\delta_m \mu^\ominus(\text{Cl}^-)$ upon transfer from pure water to pure methanol was then examined.

Even the situation with regard to transfer between pure solvents is far from satisfactory. There is an uncomfortably wide range of values and a wide variety of methods have been used for the estimation of single-ion values. Thus, Feakins et al. proposed a value for $\delta_m \mu^\ominus(\text{Cl}^-)$ of $+8.57 \text{ kcal mol}^{-1}$ ($+35.86 \text{ kJ mol}^{-1}$) at 298K (from water to pure methanol)³² and later retracted.³⁴ De Ligny and Alfenaar³¹ suggested a value of $+5.2 \text{ kcal mol}^{-1}$ ($+21.8 \text{ kJ mol}^{-1}$). Abraham³⁵ proposed a value of $+4.85 \text{ kcal mol}^{-1}$ ($+20.29 \text{ kJ mol}^{-1}$), which is based on the assumption that $\delta_m \mu^\ominus(\text{Me}_4\text{N}^+)$ is zero. This assumption has some justification in view of the large size of the Me_4N^+ cation, but it falls short because it neglects any difference in the effects of such a cation on the structure of the two solvents. Most recently, Cox and Parker³⁶ have derived a value for $\delta_m \mu^\ominus(\text{Cl}^-)$ of $+3.0 \text{ kcal mol}^{-1}$ ($+12.6 \text{ kJ mol}^{-1}$), basing their single-ion split on the more reasonable assumption that $\delta_m \mu^\ominus(\text{Ph}_4\text{As}^+) = \delta_m \mu^\ominus(\text{Ph}_4\text{B}^-)$. If the dependence of $\delta_m \mu^\ominus(\text{Cl}^-)$ on solvent composition is linear, then Cox's estimate of $\delta_m \mu^\ominus(\text{Cl}^-)$ on the transfer from water into pure methanol predicts an estimate of $\delta_m \mu^\ominus(\text{Cl}^-)$ from 50 vol.% to 70 vol.% methanol-water of $+2.5 \text{ kJ mol}^{-1}$ at 298K. Even if the dependence is not linear, one would expect only a slightly different value for $\delta_m \mu^\ominus(\text{Cl}^-)$ for this change in solvent.

The value of $\delta_m \mu^\ominus$ for the transfer of rhenium pentacarbonyl iodide from 50 vol.% to 70 vol.% methanol-water is -3.3 kJ mol^{-1} at 298.2K, while $\delta_m \mu^\ominus(\text{CN}^-)$ is about $+2.5 \text{ kJ mol}^{-1}$. These values are consistent with the observed decrease in rate for the reaction of rhenium pentacarbonyl iodide with an excess of cyanide ion upon transfer from 50 vol.% to 70 vol.% methanol-water solvent mixtures. The sum of $\delta_m \mu^\ominus$ for the two reactants is -0.8 kJ mol^{-1} , which, from the relationship

$$\delta_m \mu^\ominus = -RT \ln (k_1/k_2),$$

predicts a ratio of rate constants of 0.72, assuming $\delta_m \mu^\ominus$ (transition state) = 0. In fact the actual observed ratio is 0.12. Good agreement between the experimental and the theoretical results is hardly to be expected in view of the approximations involved. The inconsistency in the whole field is well illustrated by the fact that the use of older estimates for $\delta_m \mu^\ominus(\text{Cl}^-)$ would have given a ratio of greater than unity.

The complete field of transfer parameters of ionic species is in somewhat of a muddle and this condition is exacerbated by the inconsistencies of some workers. When there are more definitive results to be relied upon, the above approach should prove a very useful tool to investigate and make predictions about the mechanisms of reactions in various solvents and solvent mixtures.

CONCLUSION

The reactions of rhenium pentacarbonyl iodide, bromide and chloride with excess of cyanide ion in 50 vol.% and 70 vol.% methanol-water all follow a two step consecutive process, with the formation of a common product, $[\text{Re}(\text{CO})_4(\text{CN})_2]^-$. Rate laws, rate constants (Table 5.2) and, where possible, activation parameters (Table 5.3) have been determined. The first step is associative in all three cases while in the second step there is a large degree of dissociative character, again for all three rhenium pentacarbonyl halides.

$$-d[\text{Re}(\text{CO})_5\text{X}]/dt = k_{12}[\text{Re}(\text{CO})_5\text{X}][\text{CN}^-]$$

$$-d[\text{Re}(\text{CO})_4(\text{CN})\text{X}^-]/dt = \{k_{21} + k_{22}[\text{CN}^-]\}[\text{Re}(\text{CO})_4(\text{CN})\text{X}^-]$$

The Gibbs free energy of transfer of rhenium pentacarbonyl iodide, $\delta_m \mu^\ominus[\text{Re}(\text{CO})_5\text{I}]$, has been determined, from solubility measurements, as -3.3 kJ mol^{-1} , upon transfer from 50 vol.% to 70 vol.% methanol-water. The reactivity trend for the $\text{Re}(\text{CO})_5\text{I}/\text{CN}^-$ reaction, upon change of solvent medium, has been explained in terms of transfer parameters, and $\delta_m \mu^\ominus[\text{Re}(\text{CO})_5\text{I}]$ appears to control the reactivity.

TABLE 5.1 Spectroscopic data for rhenium pentacarbonyl halides in aqueous-methanol solvent mixtures

Solvent (% MeOH, v/v)	Complex	$\lambda_{\max} \frac{a}{\text{nm}}$	$\epsilon_{\max} \frac{a}{\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$	$\lambda_{\text{exp}} \frac{b}{\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$
70	Re(CO) ₅ I	330	2 x 10 ³	350
70	Re(CO) ₅ Br	320	1.6 x 10 ³	325
70	Re(CO) ₅ Cl	317	2 x 10 ³	330
50	Re(CO) ₅ I	328	2 x 10 ³	350

a Compare these values with those for Re(CO)₅X in methanol from ref. 5, Table 2 (p. 1571).

b Wavelength at which reaction with cyanide ion was actually monitored.

TABLE 5.2(a)

Observed first-order rate constants, k_{obs} , and derived rate constants, k_{12} , as defined in equation (5.4) for reaction of $\text{Re}(\text{CO})_5\text{X}$ with cyanide ion in aqueous methanol; ionic strength maintained at 2.5×10^{-2} mol dm^{-3} with potassium nitrate; mixed aqueous solvent compositions are cited by volume before mixing

<u>Re(CO)₅I</u>	Temp/K	$10^2 k_{\text{obs}}/\text{s}^{-1}$				$k_{12}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
		$10^2 [\text{KCN}]/\text{mol dm}^{-3}$				
70% methanol	293.2	-	-	1.09 ^b	1.40 ^b	0.55
	298.2	1.17	1.81	2.8	2.8	1.14 ± 0.13 ^a
	303.3	2.1	3.5	4.4	5.1	2.00 ± 0.23
	308.1	2.5	4.9	6.7	10.3	4.99 ± 0.53
50% methanol	288.7	2.4	3.5	5.0	7.8	3.56 ± 0.57
	293.2	2.8	5.1	6.1	9.8	4.43 ± 0.72

contd....

TABLE 5.2(a) (contd.)

	Temp/K	$10^2 k_{\text{obs}}/s^{-1}$	$k_{12}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
		$10^2 [\text{KCN}]/\text{mol dm}^{-3}$	
		0.5 0.75 1.0 1.25	
<u>Re(CO)₅Br</u>			
70% methanol	293.2	3.4 4.1 6.4	4.9 ± 1.1
<u>Re(CO)₅Cl</u>			
70% methanol	293.2	2.1 2.6 3.5 4.8	3.6 ± 0.5

a Standard error of the value cited.

b Similar rate constants obtained from run at isosbestic point of 301 nm (cf. text).

TABLE 5.2(b)

Observed first-order rate constants, k_{obs} , and derived rate constants, k_{21} and k_{22} , as defined in equation (5.5) for the reaction of $[Re(CO)_4(CN)X]^-$ with cyanide ion in aqueous methanol

Temp/°K	$10^4 k_{obs}/s^{-1}$					$10^4 k_{21}/s^{-1}$	$10^2 k_{22}/dm^3 mol^{-1} s^{-1}$
	1.0	1.5	2.0	2.5	2.5		
<u>Re(CO)₅I</u>							
	293.2	-	1.07	1.32	-	-	-
	298.2	1.02	1.35	1.75	2.1	0.29 ± 0.03	0.72 ± 0.016
	303.3	1.48	1.94	2.4	3.0	0.48 ± 0.1	1.00 ± 0.05
308.1	2.4	2.9	3.9	4.8	0.65 ± 0.28	1.63 ± 0.15	
70% methanol	288.7	1.19	1.67	2.0	2.5	0.34 ± 0.07	0.86 ± 0.04
	293.2	1.95	2.6	3.5	4.0	0.59 ± 0.16	1.37 ± 0.008
50% methanol							

contd...

TABLE 5.2(b) (contd.)

	Temp/K	$10^4 k_{\text{obs}}/\text{s}^{-1}$	$10^4 k_{21}/\text{s}^{-1}$	$10^2 k_{22}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
		$10^2 [\text{KCN}]/\text{mol dm}^{-3}$		
		0.5	0.75	1.0
				1.25
<u>Re(CO)₅Br</u>				
70% methanol	293.2	1.10	1.11	1.10
				1.15
				(0.06 ± 0.04)
<u>Re(CO)₅Cl</u>				
70% methanol	293.2	1.3	1.5	1.4
				1.5
				(0.19 ± 0.11)

TABLE 5.3 Activation parameters for the reaction of rhenium pentacarbonyl iodide with cyanide ion in 70 vol.% methanol-water; the subscripts correspond to those given for the rate constants in equations (5.4) and (5.5). The uncertainties quoted are the standard errors of the parameters given

	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$
First stage		
\underline{k}_{12} term	85 ± 5	$+ 38 \pm 17$
Second stage		
\underline{k}_{21} term	60 ± 7	-130 ± 25
\underline{k}_{22} term	61 ± 12	$- 84 \pm 46$

TABLE 5.4 Solubilities of rhenium pentacarbonyl halides in aqueous methanol at 293.2K

% MeOH, v/v	Solubilities/mol dm ⁻³	
	Re(CO) ₅ I	Re(CO) ₅ Br
70	3.9×10^{-3}	1.5×10^{-3}
50	1.0×10^{-3}	

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APPENDICES

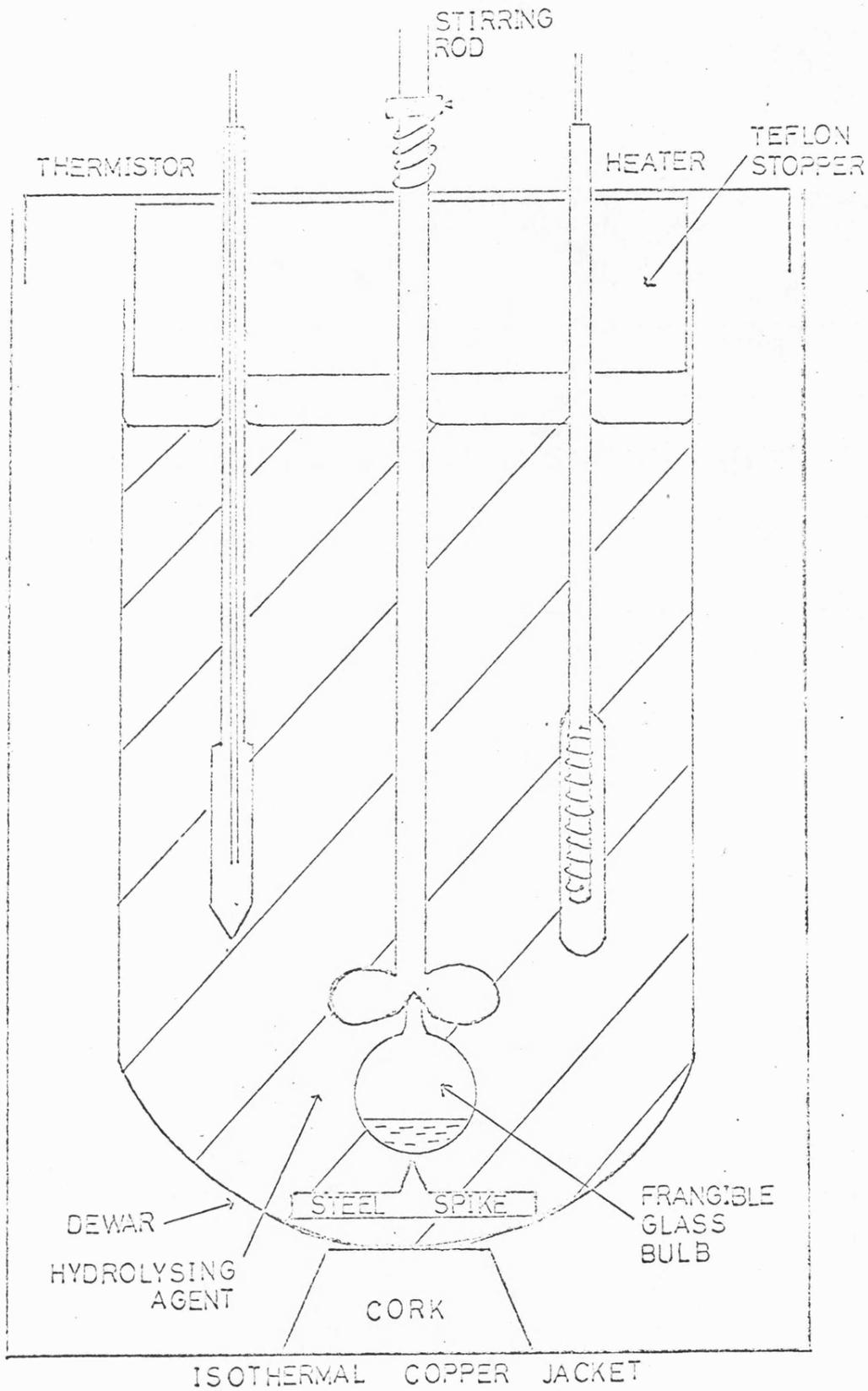
APPENDIX 1EXPERIMENTAL DETERMINATION OF
ENTHALPIES OF HYDROLYSIS

Standard enthalpies of formation of certain simple compounds, such as binary halides and oxides, may be determined directly by measuring the enthalpy change for the combination of or dissociation into the elements concerned in their standard states. For most other compounds, it is impractical to measure the standard enthalpy of formation directly and a more circuitous approach must be used. By the application of Hess's Law¹ it is possible to measure the enthalpy change of the reaction of a compound, and then one can determine the standard enthalpy of formation of the original compound from a knowledge of the stoichiometric equation of the reaction and the standard enthalpies of formation of all the other species involved in the reaction. The calorimeters used throughout the study detailed in Chapter 2 are described below.

APPARATUSFrangible Bulb Calorimeter

The assembled calorimeter is illustrated in Figure 1. The calorimeter consisted of a cylindrical Dewar vessel of

FIGURE 1



approximately 150 cm³ capacity. A teflon stopper was fabricated to fit tightly into the Dewar vessel, the stopper being surrounded by an isothermal copper shield. The teflon stopper was equipped with three equidistant holes through which were inserted a heater, a glass stirrer rod and a thermistor into the Dewar vessel. A thin-walled glass bulb (frangible bulb), containing an accurately known mass of the compound to be hydrolysed (but otherwise evacuated), was fused to the end of the glass stirrer rod. A steel spike, coated with polytetrafluoroethylene, rested at the bottom of the Dewar vessel. The assembled calorimeter was contained in a copper cylinder, which was immersed in a constant temperature water bath. The water bath was maintained at a temperature of 298.2K by the use of a heating coil, whose operation was controlled by a relay system attached to a Beckmann thermometer. To allow for the possibility of the temperature of the environment exceeding 298.2K, a copper cooling coil was incorporated in the water bath.

The temperature changes of the calorimeter's contents were detected by using a single thermistor (S.T.C. Ltd., type F, of resistance 200 ohms), which constituted one arm of a Wheatstone bridge circuit (Figure 2). The Wheatstone bridge circuit was supplied by a stabilised voltage of 1.5-4.0 volts. Large resistances were used in the ratio arms of the bridge circuit to minimise the current and thus prevent an internal heating effect in the thermistor.

A recorder (Kipp and Zonen micrograph BD 5) replaced the conventional Wheatstone bridge galvanometer and this

FIGURE 2

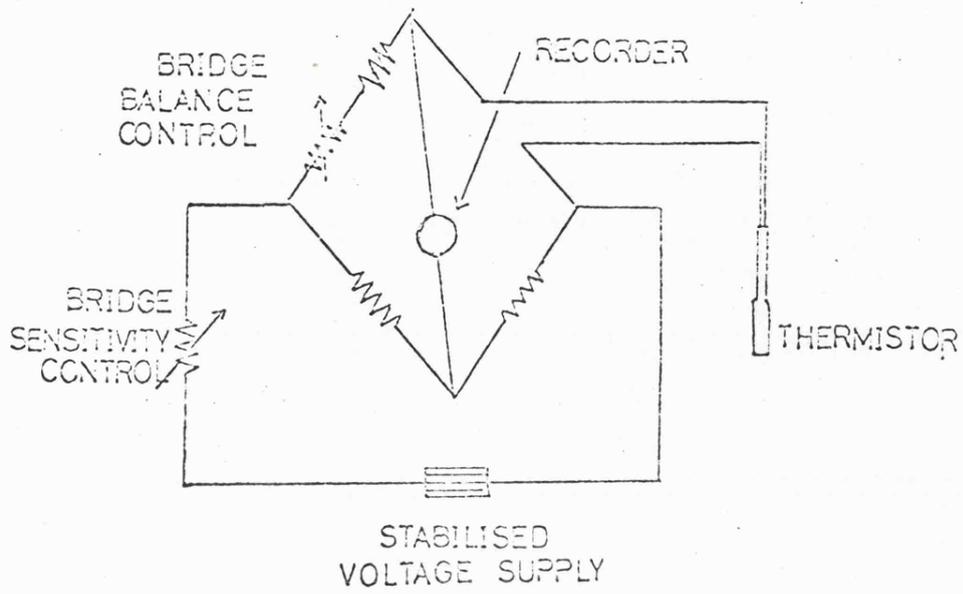
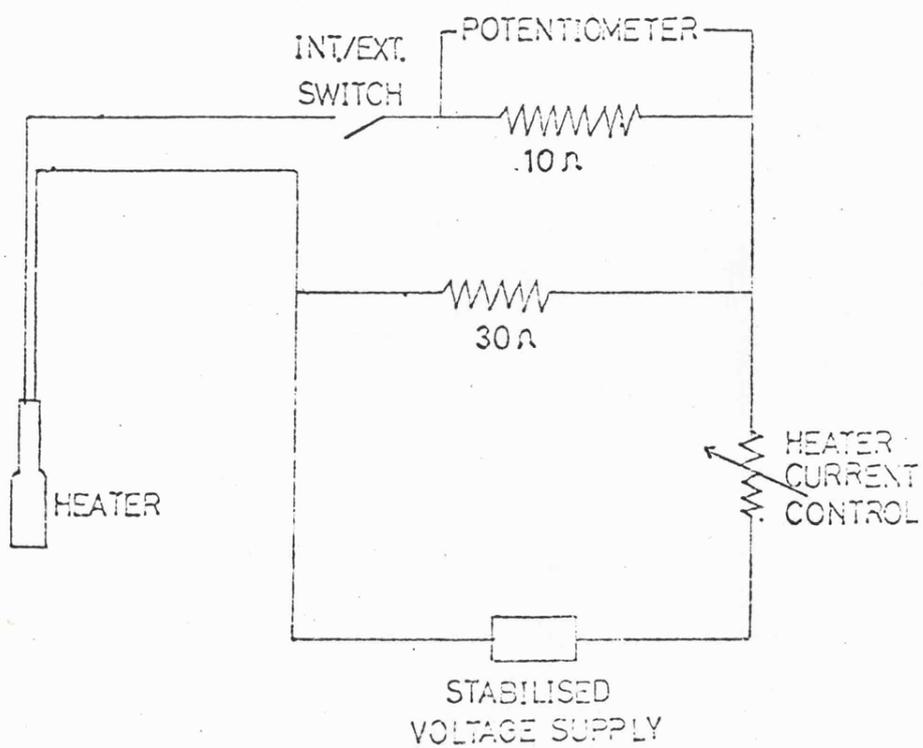


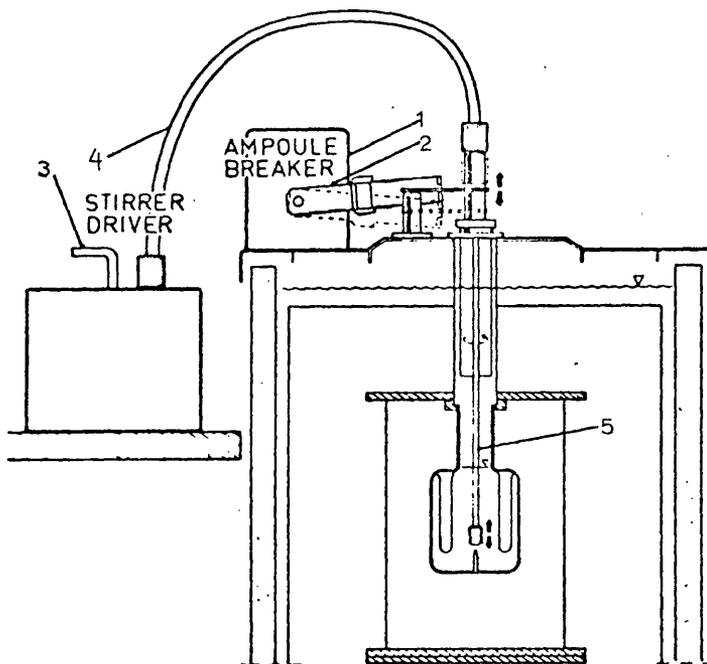
FIGURE 3



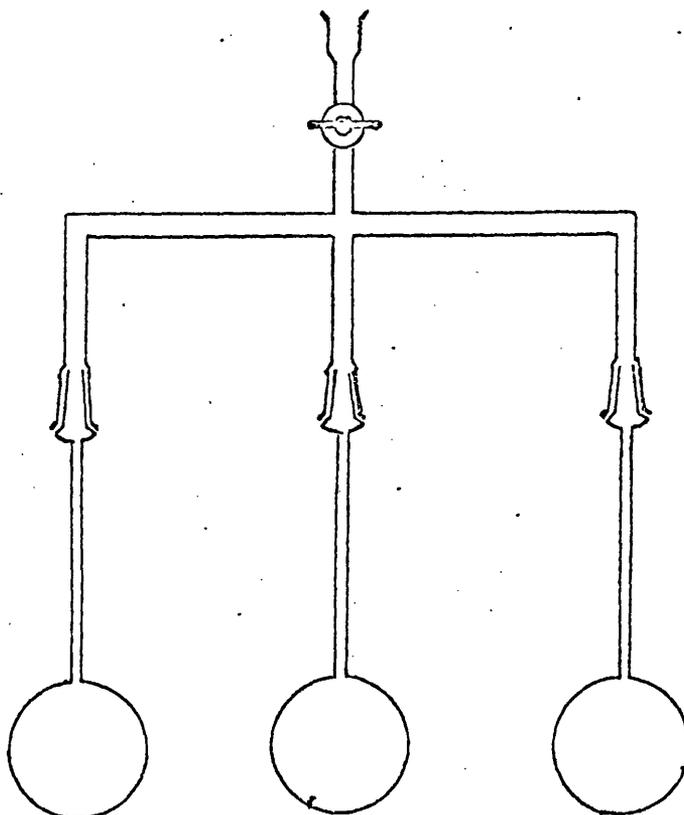
monitored the change in the balance point of the circuit, caused by the changing resistance of the thermistor with the temperature of the calorimeter's contents. The recorder was calibrated by supplying a known quantity of heat through the heater into the stirred contents of the calorimeter. The heater was fabricated by winding 38 s.w.g. 'Eureka' resistance wire round a glass tube, encasing it in an outer glass tube and sealing the joints with 'Araldite' epoxy resin. The resistance of the heater was measured accurately. The current supplied to the heater was controlled by a variable stabilised voltage supply (1.5-4.0 volts), and was determined by measuring (with a potentiometer) the potential difference across a standard 9.83 ohm resistance connected in series with the circuit (Figure 3). The current to the potentiometer was provided by a stabilised 2 volt supply.

LKB Calorimeter²

The calorimeter proper consisted of a thin-walled, 'Pyrex' glass reaction vessel of 100 cm³ capacity. This was fitted with a 2000 ohm thermistor, a 50 ohm calibration heater (a manganine coil), a sapphire-tipped rod built into the bottom of the reaction vessel, and an 18-carat gold stirrer which also served as a holder for a cylindrical glass ampoule, the whole being contained in a chromium plated brass case. The wells in which the heater and thermistor were inserted were filled with paraffin oil for good thermal contact with the calorimeter's contents (Figure 4). The thermistor formed one arm of a D.C. Wheatstone bridge. An electronic galvanometer allowed a temperature change of 5×10^{-5} °C to be detected.

FIGURE 4KEY

1. Motor for the ampoule breaker
2. Moving arm
3. Grip
4. Flexible coupling wire
5. Stirrer/ampoule holder

FIGURE 5

The chromium plated brass case was submerged in a thermostatted water bath in which the bath temperature was sensed by a thermistor and regulated by proportional heating, providing, under normal operational conditions, a temperature constancy better than 10^{-3} °C.

The calibration heater had the same function as its counterpart in the less sophisticated frangible bulb apparatus. The remaining apparatus, e.g. stabilised voltage supply for the Wheatstone bridge circuit, chart recorder, variable stabilised voltage supply for the heater circuit, potentiometer, standard resistance and voltage supply to the potentiometer, was that used for the frangible bulb calorimeter as described previously.

EXPERIMENTAL PROCEDURE

Frangible Bulb Calorimeter

Moisture-free techniques were necessary for the transfer of samples to the frangible glass bulbs. The volume of each bulb was determined accurately to allow for the mass of air in the initial weighing operation, since the bulbs were eventually sealed under a dynamic vacuum. Involatile compounds were handled in an inert atmosphere glove dry-box. The cylindrical stem of each bulb was fitted with a B7 'Quickfit' cone (Figure 5). Each set of three bulbs was attached to the 'three-forked' apparatus shown in Figure 5, and the whole arrangement was evacuated overnight and flamed out before removal to the dry-box. Involatile samples were

introduced into each of the three bulbs in the dry-box, the whole arrangement was reassembled, removed from the dry-box and again evacuated. Each bulb was then sealed off under dynamic vacuum at a point on the stem as close as possible to the spherical bulb. During the sealing-off operation, the sample in each bulb was held at 77.2K to prevent decomposition. The stems with B7 cones (after washing and drying) and the sealed bulbs (containing involatile compound in a vacuum) were weighed to constant mass. The mass of each involatile sample was calculated by the equation,

$$W = (W_2 - W_1) + \rho V$$

where,

W (g) is the mass of the sample to be hydrolysed.

W_2 (g) is the mass of the stem with cone in air, plus the evacuated bulb with sample.

W_1 (g) is the mass of the cone-stem-bulb combination in air.

ρ (g cm^{-3}) is the density of air at 298.2K.

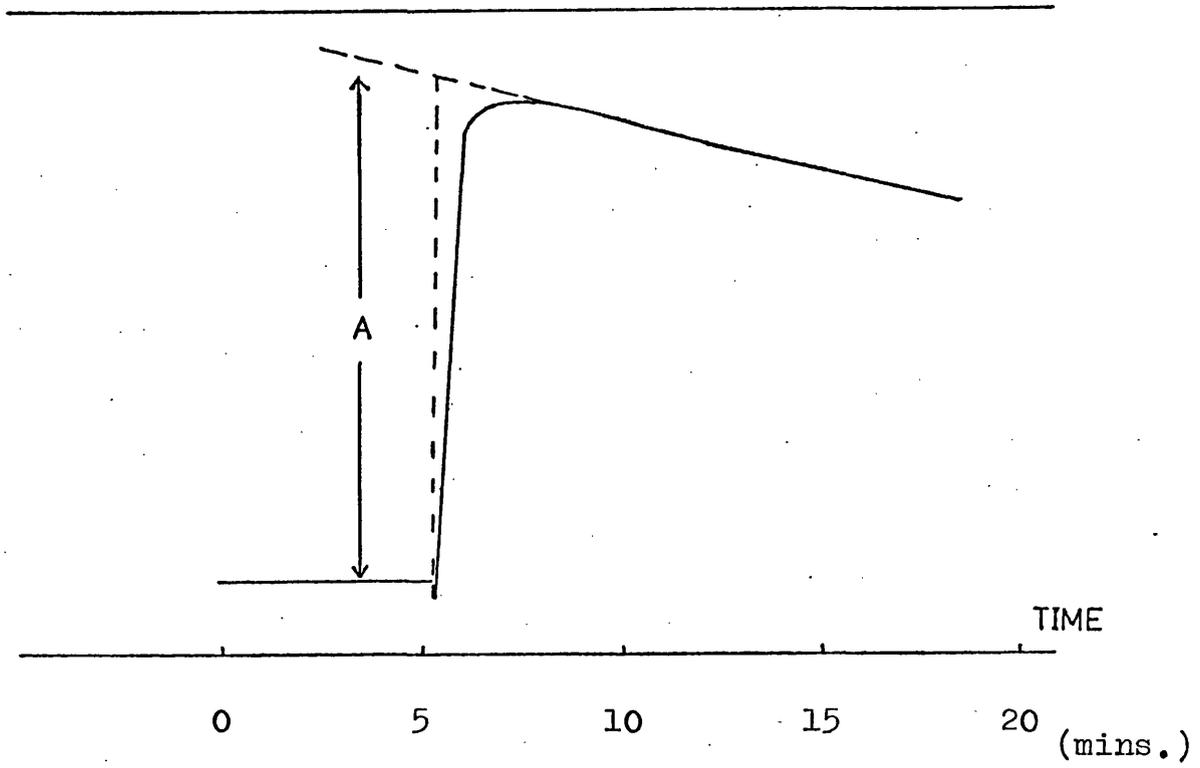
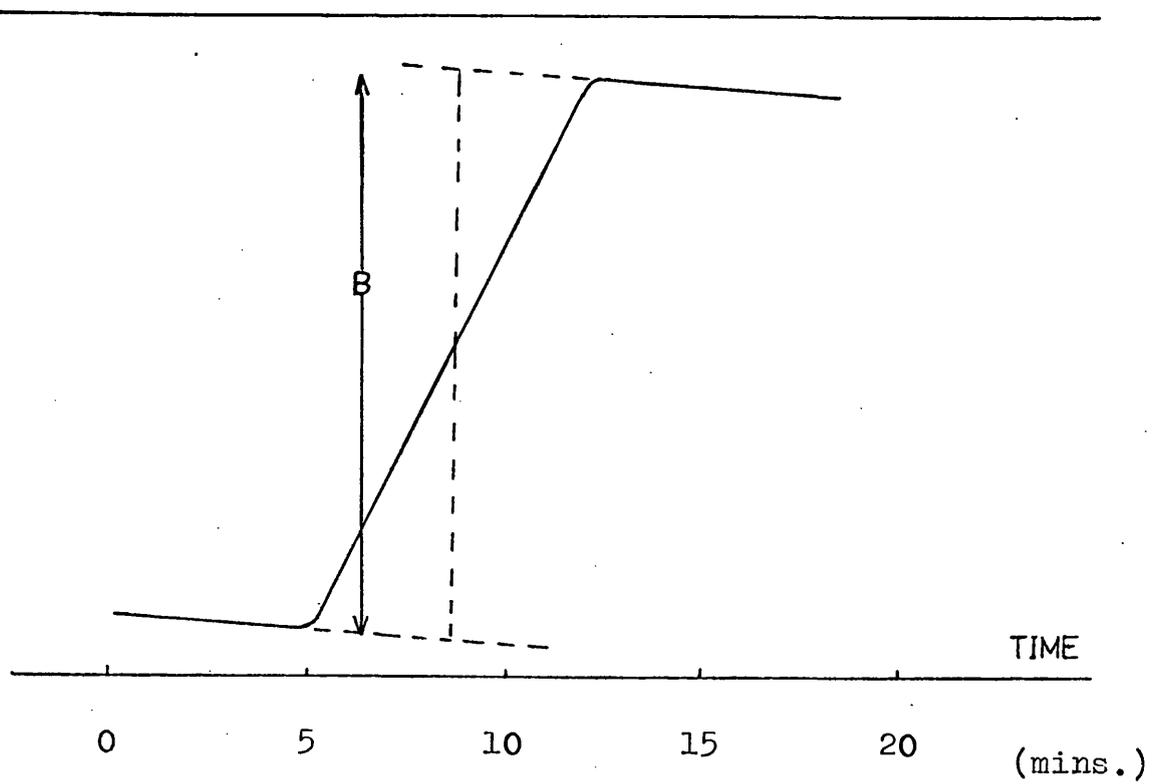
V (cm^3) is the volume of the frangible bulb.

Each sealed, evacuated bulb containing a sample was then fused to the end of a glass stirrer rod.

For compounds with rhenium in an oxidation state of +4 the hydrolysing reagent used was 2.0 molar sodium hydroxide solution under anaerobic conditions. Anaerobic sodium hydroxide solutions were used so that oxidation of $\text{ReO}_2 \cdot 2\text{H}_2\text{O}$ to ReO_4^- by dissolved oxygen was minimised. For compounds with rhenium in any other oxidation state, the hydrolysing reagent used was an excess of alkaline hypochlorite solution. Approximately 150 cm^3 of hydrolysing reagent was poured into the Dewar vessel and the calorimeter was assembled. The

solution was mixed by the stirrer rod at a constant speed controlled by an electrical stirrer motor. A minimum of twelve hours was necessary for the contents of the calorimeter to equilibrate thermally. The recorder and galvanometer were then switched on and a further two hours were allowed for the whole system to reach equilibrium. When no deviations in the recorder trace were observable, the glass stirrer rod was depressed causing the glass bulb to shatter on the steel spike. The change in temperature as the hydrolysis proceeded was monitored by the thermistor and displayed as a deflection on the recorder's chart. A cooling curve was then plotted for approximately twenty minutes after the reaction had finished. The cooling curve was extrapolated back to the first instant of reaction (the shattering of the bulb), and the vertical distance between the two lines at this point corresponded to the heat change in the reaction. Figure 6 illustrates a typical exothermic hydrolysis deflection.

The recorder was then calibrated by introducing a known quantity of heat into the calorimeter by means of the heater. The resistance of the heater had previously been measured accurately. The recorder pen was activated five minutes before switching on the heater and the length of time the heater remained in operation was measured accurately to 0.1 second with a Junghan's stop-watch. Midway through the calibration the heater current was measured. A cooling curve was plotted for approximately fifteen minutes after the deactivation of the heater circuit. The two curves were extrapolated to the point corresponding to the time of measuring the heater current. The vertical distance

FIGURE 6FIGURE 7

between the two extrapolated lines at this point corresponded to the heat supplied. Two calibrations were run for each individual hydrolysis experiment, to minimise errors.

The enthalpy change for the reaction of a compound thus monitored is given by the equation:

$$\Delta H = \frac{I^2 \cdot R \cdot T}{10^3} \times \frac{Y}{Z} \times \frac{M}{W} \quad \text{kJ mol}^{-1}$$

where,

I (A) is the average current measured midway through the calibration.

R (Ω) is the heater resistance.

T (s) is the time during which the heater current was supplied.

Y (mm) is the deflection observed for the reaction.

Z (mm) is the deflection observed for the calibration.

M is the molecular weight of the compound.

W (g) is the mass of the sample in the evacuated bulb.

A typical calibration curve is illustrated in Figure 7.

The reliability of the apparatus was checked periodically by the measurement of the enthalpy of solution of tris(hydroxymethyl)methylamine (THAM or TRIS). The enthalpy of solution of a known mass of sample (which was first dried overnight at 343K) was measured directly in 0.1 molar hydrochloric acid. Typical runs gave answers of, for example, -30.00, -30.56 and -29.58 kJ mol⁻¹. These results were consistent with the literature value³ of -29.74 kJ mol⁻¹.

LKB Calorimeter

The small ampoules, of 1 cm³ capacity and shaped like the heads of mallets, used with the LKB precision calorimeter were difficult to evacuate effectively. The ampoules were dried overnight at 343K and then quickly transferred to a dry-box. The dry-box was large enough to contain a balance. The moisture-sensitive samples already in the dry-box were introduced carefully into the small ampoules and then the ampoules were cleaned with tissues, weighed, sealed by silicon rubber stoppers and microwax, removed from the dry-box and placed in the calorimeter reaction vessel. Obviously, for the moisture- and air-stable compounds, it was not necessary to fill, weigh and seal the ampoules inside the dry-box. Again, the hydrolysing reagent needed to be anaerobic for the hydrolyses of the rhenium(IV) compounds. Due to the premature thermostating of the hydrolysis reagent in the reaction vessel and to the design of the calorimeter and water bath, only 30 minutes were required to achieve thermal equilibration.

The reaction was initiated by activating a motor-driven mechanism, which broke the thin end-walls of the sample ampoule against the sapphire-tipped rod built into the bottom of the reaction vessel. The monitoring and recording of the enthalpy changes for the reaction and calibration runs, and the calculation of the enthalpies of hydrolysis, were identical to the procedure already described for the frangible bulb apparatus.

The reliability of the apparatus was checked by the measurement of the solution enthalpy of TRIS samples, and the results were found to be consistent with the literature value.³

EXPERIMENTAL ACCURACY

Frangible Bulb Calorimeter

The thermistor used to monitor the temperature changes was well suited to the apparatus because of its low heat capacity and its compact size. Although the errors resulting from the use of the thermistor were likely to be minimal, the circuit incorporating the thermistor has been estimated as producing an error of 1% in the recorded deflection.

The measurement of the deflections required the extrapolation of the recorded cooling curves. The compounds used in the apparatus hydrolysed very rapidly (except for the slightly slower β -rhenium tetrachloride) and thus the error in the measurement of deflections was very small ($< \frac{1}{2}\%$). Moreover, the mass of the sample, the heat dissipated in the calibration and the scale of the recorder were all chosen to give a maximum deflection on the chart and thus reduce the error in the physical measurement of the chart traces.

Errors arising from the measurement of the heater current during calibrations were small. The heater current was

calculated by measuring the potential difference across a standard 9.83 ohm resistance. The magnitude of the current was generally in the region of 0.1-0.15 amps, measured to an accuracy of 0.0001 amps, and varied by no more than 0.0005 amps during any one calibration.

The enthalpies of hydrolysis were measured at 298.2K. Errors arising from temperature variation of the environment were small, since the whole calorimeter assembly was immersed in an automatically controlled water bath, and the maximum observed variation was 0.1 °C.

LKB Calorimeter

The precision of the unit was such that for electrical calibration, using 83.7 joules, the standard deviation of the calibration constant was 0.01% or less, e.g. this represents uncertainty limits of 8.4 mJ.

The inability to protect the dried ampoules from moisture during transfer to the dry-box, and indeed from traces of moisture in the dry-box itself, caused some error in the results for the moisture-sensitive compounds. However, the speed with which the ampoules were filled, weighed and sealed, and the speed with which the sample reacted in the calorimeter, prevented the errors from this source exceeding more than about 1%. The other errors manifested in the results for the moisture-sensitive compounds arose mainly from the difficulty of weighing to four decimal place accuracy. This inaccuracy probably accounted for errors of about 1-2% in the measurement of the enthalpies of hydrolysis. It was for this reason that

the runs of the moisture-sensitive samples on the LKB were duplicated on the frangible bulb apparatus. Until a method can be devised for excluding moisture more effectively from the glass ampoules, the LKB calorimetry apparatus will remain of use primarily for the reactions of moisture- and air-stable compounds. The advantages of using the LKB apparatus are its precision and the number of runs one can do in any one day, when dealing with air-stable compounds.

In all the hydrolyses, it was necessary to use a large excess of hydrolysing reagent, so that the change in dilution of the reagent upon reaction was minimised. It was then possible to use constant enthalpies of formation for the reagents, $\text{OH}^- (\text{aq})$ and $\text{OCl}^- (\text{aq})$, without introducing errors due to the enthalpies of dilution.

APPENDIX 3a

Basic programme for the calculation of standard deviation, standard error of the mean and 90% confidence limits for a series of N measurements of a quantity, X

```

5 DIM X(99)
6 REM WHEN N=5,T=2.13  N=6,T=2.02  N=7,T=1.94  N=8,T=1.90  N=9,T=1.86
7 REM WHEN N=10,T=1.83
10 LET S1 = 0
20 LET S2=0
30 READ N
40 PRINT "N="N
50 FOR I=1 TO N
60 READ X(I)
70 PRINT "X"(I)="X(I)
80 NEXT I
90 FOR I=1 TO N
100 LET S1=S1+X(I)
110 NEXT I
120 PRINT "SUM="S1
130 LET A=S1/N
140 PRINT"MEAN="A
150 FOR I=1 TO N
160 LET B=X(I)-A
170 GOSUB 340
175 LET S2=S2+V+2+B+2
180 NEXT I
190 PRINT"S2="S2
200 LET T=SQR(S2/N)
210 PRINT "STANDARD DEVIATION="T
211 PRINT"STANDARD ERROR OF MEAN="T/SQR(N)
212 PRINT"90 PER CENT CONFIDENCE LIMITS=T*SEM"
310 DATA8
320 DATA170.6,167.5,181.7,167.4,172.6,171.1,170.9,175.3
325 DATA1.9
330 STOP
340 IF B=0 THEN 350
345 GOTO 380
350 PRINT"ZERO"
370 RETURN
380 IF B<0 THEN 390
385 GOTO 430
390 LET V=-B
399 LET B=1E-9
400 PRINT V+2"=V+2"
410 RETURN
430 PRINTB+2"=B+2"
431 LET V=1E-9
460 RETURN

```

SUBPROGS	CODE		CONSTANT		LOCAL WKSPACE		DYNAMIC ARRAYS
	START	LENGTH	START	LENGTH	START	LENGTH	
ORTDS1	0	8	5906	2	9886	0	0
ZZZZY	0	8	5910	2	9886	0	0
SEGMENT LENGTH		16					
AXEQB	0	453	5914	18	9886	30	36
EIGEN	0	1005	5938	50	9916	80	48
PRELIM	0	1903	6004	682	9996	26	18
PRIME	0	155	6688	50	10022	7	0
SEGMENT LENGTH		3516					
BOND	0	1721	6760	266	10029	56	172
F800	0	716	7028	210	10085	37	15
SEGMENT LENGTH		2437					
F700	0	1987	7240	466	10122	52	24
SEGMENT LENGTH		1987					
F400	0	313	7712	50	10174	29	0
SEARC	0	1958	7762	450	10203	110	866
STOR	0	133	8212	18	10313	8	0
SEGMENT LENGTH		2404					
MAINPROG	21237	751	8248	818	10321	22	0
ARCCOS	21189	48	9066	18	10343	3	0
ATOM	20929	260	9084	34	10346	18	6
AXES	20727	202	9118	34	10364	18	18
DIFV	20686	41	9152	2	10382	10	0
DROR	20581	105	9156	10	10392	11	6
ERPNT	20565	16	9166	26	10403	2	0
F200	20477	88	9196	42	10405	7	0
F500	19898	579	9238	66	10412	22	42
F600	19279	619	9304	50	10434	29	29
F900	18696	583	9354	74	10463	44	48
MM	18613	83	9428	10	10507	16	0
MV	18547	66	9438	10	10523	13	0
NORM	18434	113	9448	18	10536	21	6
PAXES	18156	278	9468	42	10557	16	6
PLTXY	18020	136	9510	26	10573	13	0
PROJ	17899	121	9536	10	10586	26	0
RADIAL	17743	156	9546	18	10612	15	0
TMM	17653	90	9564	10	10627	22	0
UNIT	17405	248	9574	10	10649	36	6
VM	17339	66	9584	10	10685	13	0
VMV	17256	81	9594	10	10698	23	0
VV	17210	48	9604	10	10721	16	0
XYZ	17036	174	9614	18	10737	16	0
F1000	17028	8	9632	2	10753	0	0
SPARE	17020	8	9634	2	10753	1	0
PLOT	16963	57	9638	18	10754	14	0
SIMBOL	16834	129	9660	50	10768	19	3
BUFFER	16808	26	9712	14	0	0	0
SGTRAC	16664	144	9728	50	0	0	0
ORIGIN	16648	16	9780	10	10787	5	0
MOVE	16632	16	9790	10	10792	5	0
DRAW	16616	16	9800	10	10797	5	0
WAY	16600	16	9810	10	10802	5	0
CENCH	16584	16	9820	10	10807	6	0
PLOTPK	16374	210	9832	54	0	0	0

APPENDIX 3c Basic least-mean squares programme for the calculation of observed first-order rate constants, k_{obs} , from the decrease in absorption with time

```

5 CLOSE 3
6 OPEN "KB:"AS FILE 3
8 DIM X(30),Y(30),A(30),E(30)
9 DIM W(30)
10 LET S1=0:LET S2=0:LET S3=0:LET S4=0:LET L=0
11 PRINT "UNIT TIME INTERVAL=";
12 INPUT #3,Q
18 PRINT "NO. POINTS =";
19 INPUT #3,N
20 FOR I=1TON
22 LET X(I)=I
23 NEXT I
24 FOR I=1TON
25 PRINT "Y(";I;")=";
26 INPUT #3,Y(I)
27 NEXT I
28 GOSUB 200
29 GOTO34
30 PRINT "FOR SAME DATA, PRINT:GOTO34:"
31 PRINT "FOR DIFF. DATA, PRINT:GOTO28:"
32 PRINT " TO STOP,PRINT :GOTO365:"
33 STOP
34 LET L=0
35 PRINT "RANGE INF. +STEP=";
36 INPUT #3,P,R,0
40 FOR W=P TO R STEP 0
45 FOR I=Z TO V
47 LET X=X(I)
48 LET Y=Y(I)
49 LET Y=LOG(Y-W)
55 LET S1=S1+X
56 LET S2=S2+Y
57 LET S3=S3+X*Y
58 LET S4=S4+X*X
59 NEXT I
61 LET G=(V-(Z-1))
62 LET C=1/(G*S4-S1*S1)
63 LET A=(G*S3-S1*S2)*C
64 LET B=(S4*S2-S1*S3)*C
68 FOR I=Z TO V
70 LET D2=A*X(I)+B-LOG(Y(I)-W)
75 LET D=D+D2*D2
80 NEXT I
85 LET D=D*C/(G-2)
88 LET E=(SQR(G*D))/(-1*A)*100
90 LET L=L+1
91 LET E(L)=E
92 LET A(L)=A
93 LET W(L)=W
100 LET S1=0:LET S2=0:LET S3=0:LET S4=0:LET D=0
102 NEXT W
103 LET H=L
104 GOSUB 250
110 GOTO30
200 PRINT "1ST I VALUE =";
205 INPUT #3,Z
210 PRINT "LAST I VALUE =";
215 INPUT #3,V
220 RETURN
250 FOR L=2 TO H
253 PRINT "H=";H
255 IF E(L)<E(L-1) THEN 305
256 PRINT E(L),E(L-1)
258 NEXT L
259 PRINT "NO MINIMUM IN THIS RANGE...."
300 PRINT
303 GOTO34
305 IF E(L)<E(L+1) THEN 350
307 PRINT E(L),E(L+1)
310 GOTO250
350 FOR I=1TO3
351 PRINT CHR$(7)
352 NEXT I
353 PRINT " ANSWERS ARE....."
354 PRINT
355 PRINT "      K-OBS=";-A(L)/Q,"      % ERROR= ";E(L)
356 PRINT"      -----"
357 PRINT
358 PRINT "INFINITY=";W(L),"*****"
360 RETURN
365 STOP

```

APPENDIX 3d Basic least-mean-squares straight-line programme for the calculation of second-order rate constants, k_2 , from the dependence of observed first-order rate constants, k_{obs} , on the molar concentration of catalyst

```

5 CLOSE3
6 OPEN"KB:"ASFILE3
10 DIMX(20),Y(20)
21 LET S1=0:LETS2=0:LETS3=0:LETS4=0
23 LETD=0
26 PRINT "BEST STRAIGHT LINE X VS Y"
29 PRINT "NO.OF POINTS=";
30 INPUT #3,N
40 FOR I=1 TO N
45 PRINT"X(";I;")=";
52 INPUT#3,X
53 PRINT"Y(";I;")=";
54 INPUT#3,Y
55 LET X(I)=X
56 LET Y(I)=Y
60 LETS1=S1+X
70 LETS2=S2+Y
80 LETS3=S3+X*Y
90 LETS4=S4+X*X
100 NEXT I
110 LETC=1/(N*S4-S1*S1)
120 LETA=(N*S3-S1*S2)*C
130 LETB=(S4*S2-S1*S3)*C
140 FOR I=1TON
150 LET D2=A*X(I)+B-Y(I):LET D=D+D2*D2
160 NEXT I
165 LETD=D*C/(N-2)
170 PRINT"Y(;"A;"#";SQR(N*D);")X+";B;"#";SQR(S4*D)
180 STOP

```

APPENDIX 3e Basic least-mean-squares programme for the calculation of activation energies from the dependence of $\log k_2$ on $\frac{1}{T}$

```

5 CLOSE3
6 OPEN"KB:"ASFILE3
10 DIM X(27),Y(27)
21 LET S1=0:LETS2=0:LETS3=0:LETS4=0
23 LETD=0
28 PRINT "ARRHENIUS, J.C./////"
29 PRINT "NO.OF POINTS=";
30 INPUT #3,N
35 PRINT "X IS TEMP. INCENTIGRADE, Y IS K"
40 FOR I=1 TO N
45 PRINT"X(";I;")=";
52 INPUT#3,X
53 PRINT"Y(";I;")=";
54 INPUT#3,Y
55 LET X=1000/(X+273.16)
56 LET X(I)=X
57 LET Y=LOG(Y)/2.302585
58 LET Y(I)=Y
60 LETS1=S1+X
70 LETS2=S2+Y
80 LETS3=S3+X*Y
90 LETS4=S4+X*X
100 NEXT I
110 LETC=1/(N*S4-S1*S1)
120 LETA=(N*S3-S1*S2)*C
130 LETB=(S4*S2-S1*S3)*C
140 FOR I=1TON
150 LET D2=A*X(I)+B-Y(I):LET D=D+D2*D2
160 NEXT I
165 LETD=D*C/(N-2)
170 PRINT"Y=(;A;#" ;SQR(N*D);)X+;B;#" ;SQR(S4*D)
171 PRINT"ACTIVATION ENERGY=";-4.57563*A;#"4.57563*SQR(N*D); "KCAL"
172 PRINT"A FACTOR IS 10^;B;#" ;SQR(S4*D)
180 STOP

```

```
&JOB;CH001050MJE16;
```

```
&ALGOL;
LIBRARY
ALGOL
```

```
&LIST;
```

```

1  INCHM;
2  "BEGIN"
3  "INTEGER" I,J,N;
4  JA,TE,KK;
5  W, VV, CONT, V;
6  JB,
7  K, NC;
8  "REAL" TS, TNEW, DIFF, TH, TH;
9  RAT;
10 SA, SB, SC, QD;
11 R;
12 TC, DUMMY, EX, SEK1, SEK2, SEEB;
13 "ARRAY" T[1:500], G[1:2, 1:500],
14 DK1, DK2, DEB, A0, K1G;
15 K2G, EBG[1:10];
16 K1, K2, EB[1:51],
17 EC, EA,
18 DDK1R, DDBR, DDEBR, P, DCALC, DELTAD;
19 DDELTA,
20 DDK1, DDK2, DDEB[1:500],
21 C, A[1:3, 1:3], B[1:4, 1:4];
22
23
24 "PROCEDURE" MXCOPY(B, A, W);
25 "INTEGER" W;
26 "ARRAY" A, B;
27 "BEGIN"
28 "INTEGER" U, S;
29 "FOR" Q:=1 "STEP" 1 "UNTIL" W "DO"
30 "FOR" S:=1 "STEP" 1 "UNTIL" W "DO"
31 B[Q, S]:= A[U, S];
32 "END" MXCOPY;
33
34 "PROCEDURE" INVMX(B, W);
35 "INTEGER" W;
36 "ARRAY" B;
37 "BEGIN"
38 "REAL" MAX, EPS;
39 "INTEGER" S, L, V, Z, R;
40 R:=W;
41 EPS:=2.0*10-37;
42 "BEGIN"
43 "INTEGER" "ARRAY" RR, BR[1:R];
44 "FOR" SS:=1 "STEP" 1 "UNTIL" R "DO"
45 "BEGIN"
```

```

46 MAX:=0;
47 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
48 "BEGIN"
49 "FOR" V:=1 "STEP" 1 "UNTIL" SS-1 "DO"
50 "IF" L=BR[V] "THEN" "GOTO" L1;
51 "IF" ABS(MAX)-ABS(BCL,1))
52 "LE" 0 "THEN"
53 "BEGIN"
54 BR[SS]:=L;
55 MAX:= BCL,1);
56 "END";
57 L1: "END";
58 "IF" ABS(MAX)<EPS "THEN"
59 "BEGIN"
60 "PRINT" 'L\ INVMX ERROR';
61 STOP;
62 "END";
63 V:= BR[SS];
64 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
65 BCL,R+1):="IF"L=V "THEN" 1 "ELSE" 0;
66 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
67 BC[V,L]:=B[V,L+1]/MAX;
68 "FOR" L:=1 "STEP" 1 "UNTIL" R "DO"
69 "BEGIN"
70 MAX:= BCL,1);
71 "IF" L "NE" V "THEN" "FOR" Z:=1 "STEP" 1 "UNTIL" R "DO"
72 BCL,Z):= BCL,Z+1)-MAX*BC[V,Z]
73 "END"
74 "END";
75 "FOR" Z:=1 "STEP" 1 "UNTIL" R "DO"
76 RR[Z]:=Z;
77 "FOR" Z:=1 "STEP" 1 "UNTIL" R-1 "DO"
78 "BEGIN"
79 "IF" BR[Z]=RR[Z] "THEN" "GOTO" LOOP "ELSE"
80 "FOR" L:= 7+1 "STEP" 1 "UNTIL" R "DO"
81 "IF" RR[L]= BR[Z] "THEN" "GOTO" SWOP;
82 SWOP: "FOR" V:=1 "STEP" 1 "UNTIL" R "DO"
83 "BEGIN"
84 MAX:=BC[Z,V];
85 BC[Z,V]:=BCL,V);
86 BCL,V):=MAX
87 "END";
88 RR[L]:=RR[Z];
89 LOOP:"END";
90 "FOR" Z:=1 "STEP" 1 "UNTIL" R-1 "DO"
91 "BEGIN"
92 "FOR" L:=Z "STEP" 1 "UNTIL" R "DO"
93 "IF" BR[L]=Z "THEN"
94 "BEGIN"
95 "IF" Z=L "THEN" "GOTO" OUT
96 ;
97 "FOR" V:=1 "STEP" 1 "UNTIL" R "DO"
98 "BEGIN"
99 MAX:=BC[V,Z];
100 BC[V,Z]:=B[V,L];
101 BC[V,L]:=MAX;"END";
102 BR[L]:=BR[Z]
103 "END";
104 OUT: "END"
105 "END";

```

```

106 "END" IVMHX;
107
108
109 "PROCEDURE" MXPROD(C,A,B,W);
110 "INTEGER" W;
111 "ARRAY" A,B,C;"BEGIN"
112 "INTEGER" I,J,K;
113 "FOR" I:=1"STEP"1"UNTIL"W"DO"
114 "FOR" J:=1"STEP"1"UNTIL"W"DO"
115 "BEGIN"
116 C[I,J]:=0;
117 "FOR" K:=1"STEP"1"UNTIL"W"DO"
118 C[I,J]:=C[I,J]+A[I,K]*B[K,J];
119 "END";
120 "END" MXPROD;
121
122 "PROCEDURE" PRINTMX(C,N);
123 "INTEGER" N;
124 "ARRAY" C;
125 "BEGIN"
126 "INTEGER" I,J,K,L,M,MM;
127 "INTEGER" "ARRAY" LIM[0:7];
128 FREEPOINT (11); DIGITS(3);
129 I:=N "DIV" 9;
130 LIM[0]:=N-9*I;
131 K:=0;
132 "FOR" J:=1 "STEP" 1 "UNTIL" I "DO" LIM[J];=9;
133 "FOR" J:=I "STEP" -1 "UNTIL" 0 "DO"
134 "BEGIN"
135 "PRINT" 'L',S6;
136 "IF" LIM[J] > 0 "THEN" "BEGIN"
137 "FOR" L:=1 "STEP" 1 "UNTIL" LIM[J] "DO"
138 "PRINT" SAMELINE ,DIGITS (7),L+K,'S5';
139 "FOR" M:=1 "STEP" 1 "UNTIL" N "DO"
140 "BEGIN"
141 "PRINT" 'L',SAMELINE,DIGITS(2),'S3', M;
142 "FOR" MM:=K+1 "STEP" 1 "UNTIL" K+LIM[J] "DO"
143 "PRINT" SAMELINE,SCALED(2),C[M,MM];
144 "END";
145 K:=K+9; "PRINT" 'L';
146 "END" ;
147 "END";
148 "END" PRINTMX;
149
150 "PROCEDURE" IXSET;
151 "BEGIN"
152 "PRINT"'L';
153 "COMMENT"R>0.01;
154 "FOR" I:=1"STEP"1"UNTIL"K"DO""BEGIN"
155 "IF" T[C]=0"THEN""GOTO"POOLE;
156 DDK1[C]:=((E[B]-E[C])/(K1[C]-K2[C])+2)*((K1[C]-K2[C])*
157 (EXP(-K2[C]*T[C])-EXP(-K1[C]*T[C])+K1[C]*T[C]*EXP(-K1[C]*
158 -K1[C]*(EXP(-K2[C]*T[C])-EXP(-K1[C]*T[C])))
159 -T[C]*(E[A]-E[C])*EXP(-K1[C]*T[C]));
160 DDK2[C]:=((K1[C]*(E[B]-E[C]))/(K1[C]-K2[C])+2)
161 *((EXP(-K2[C]*T[C])-EXP(-K1[C]*T[C])-(K1[C]-K2[C])*T[C]
162 *EXP(-K2[C]*T[C]));
163 DDEB[C]:=K1[C]*(EXP(-K2[C]*T[C])-
164 EXP(-K1[C]*T[C]))/(K1[C]-K2[C]);
165 POOLE:"END";"END"IXSET;

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166
167
168
169 "PROCEDURE" IXSETUP;
170 "BEGIN"
171 "COMMENT"R<0.01;
172 "FOR" I:=1"STEP"1"UNTIL"K"DO""BEGIN"
173 "PRINT" 'L';
174 "IF"TC[I]=0"THEN""GOTO"SOTON;
175 R:=(K1[W]-K2[W])/K1[W];
176 DDK1RC[I]:=(EXP(-K1[W]*TC[I]))*(EB[W]-EC[W])*(TC[I]+R*K1[W]*TC[I]+2
177 (R+2*K1[W]+2*TC[I]+3/2)+
178 ((R+3*K1[W]+3*TC[I]+4)/6))
179 -TC[I]*((K1[W]*TC[I])+
180 ((R*K1[W]+2*TC[I]+2)/2)
181 +((R+2*K1[W]+3*TC[I]+3)/6)
182 +((R+3*K1[W]+4*TC[I]+4)/24))
183 -TC[I]*(EXP(-K1[W]*TC[I]))*(EA[W]-EB[W]);
184 DDDR[EI]:=(EB[W]-EC[W])*(EXP(-K1[W]*TC[I]))*(((K1[W]+2*TC[I]+2)/2)
185 +((R*K1[W]+3*TC[I]+3)/3)
186 +((R+2*K1[W]+4*TC[I]+4)/8));
187 DDK1[EI]:=DDK1RC[I]+(DDDR[EI]*K2[W]/K1[W]+2);
188 DDK2[EI]:=DDDR[EI]*(-1/K1[EI]);
189 DDEB[EI]:=(EXP(-K1[W]*TC[I]))*(K1[W]*TC[I]+((R*K1[W]+2*TC[I]+2)/2)
190 +((R+2*K1[W]+3*TC[I]+3)/6)
191 +((R+3*K1[W]+4*TC[I]+4)/24));
192 "PRINT" SAMELINE, SCALED(9), KK, 'S3', TC[KK], 'S3';
193 "PRINT" SAMELINE, SCALED(9), K, 'S2';
194 DDK1[EI], 'S2', DDK2[EI], 'S2', DDEB[EI], 'L';
195 SOTON: "END"; "END";
196
197
198
199
200 "PROCEDURE" IXMAKE;
201 "BEGIN"
202 "PRINT" 'L';
203 "FOR" I:=1"STEP"1"UNTIL"3"DO"
204 "FOR" J:=1 "STEP" 1 "UNTIL" 3 "DO"
205 A[I, J]:=0;
206 "FOR" I:=1"STEP"1"UNTIL"K"DO""BEGIN"
207 "IF"TC[I]=0"THEN""GOTO"LONDON;
208 A[1,1]:=A[1,1]+((DDK1[EI])+2);
209 A[1,2]:=A[1,2]+(DDK1[EI]*DDK2[EI]);
210 A[1,3]:=A[1,3]+(DDK1[EI]*DDEB[EI]);
211 A[2,2]:= A[2,2]+((DDK2[EI])+2);
212 A[2,3]:=A[2,3]+(DDK2[EI]*DDEB[EI]);
213 A[3,3]:=A[3,3]+(DDDR[EI])+2);
214 LONDON: "END";
215 A[2,1]:=A[1,2];
216 A[3,1]:=A[1,3];
217 A[3,2]:=A[2,3];
218 "END";
219
220 "PROCEDURE" COLUMN;
221 "BEGIN"
222 SA:=SB:=SC:=0;
223 JA:=1;
224 "FOR" I:=1"STEP" 1"UNTIL" K"DO""BEGIN"
225 "IF"TC[I]=0"THEN""GOTO"NEWYORK;

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226 DCALC[I]:=(EACW]-EC[W]) * EXP(-K1[W]*TC[I])
227 +(((EBCW]-EC[W]) *
228 K1[W] * (EXP(-K2[W]*TC[I]) - EXP(-K1[W]*TC[I])) / (K1[W]-K2[W])) + EC[W];
229 DELTAD[I]:=PC[I]-DCALC[I];
230 SA:=SA+DELTAD[I]*DDK1[I];
231 SB:=SB+DELTAD[I]*DDK2[I];
232 SC:=SC+DELTAD[I]*DDER[I];
233 JB:=10*JA;
234 "IF" I=JE"THEN" "BEGIN"
235 "PRINT" 'L',SAMELINE,SCALED(9),I,'S2',SA,'S2',
236 SB,'S2',SC,'S2',DCALC[I],'S2',DELTAD[I];
237 "PRINT" SAMELINE,SCALED(9),'S3',PC[I];
238 JA:=JA+3;
239 "END";
240 NEWYORK:"END";"END";
241
242 "PRINT" 'F'ANALYSIS FOR RATE DATA FROM SPECTRA';
243 "PRINT" 'I'UNIVERSITY OF LEICESTER***M.J,BLANDAMER';
244 TE:=0;
245 "PRINT" 'I'SYSTEM';
246 "PRINT" 'I4';
247 "READ" IC;
248 "READ"K;
249 "PRINT" 'L'NO CELLS=',SAMELINE,SCALED(9),NC;
250 "FOR" W:=1 "STEP" 1 "UNTIL"NC "DO"
251 "BEGIN"
252 "READ"AO[W],K1G[W],K2G[W],EBG[W],EAC[W],EC[W];
253 "COMMENT" G MEANS GUESSED****
254 ***AO,EA,FC,ARE KNOWN;
255 "PRINT" 'L',SAMELINE,SCALED(9),AO[W],'S3',
256 K1G[W],'S3',K2G[W],
257 'S3',EBG[W],'S3',EAC[I],'S3',EC[W];
258 "END";
259 "FOR" I:=1"STEP"1"UNTIL"K"DO""BEGIN"
260 "READ"TC[I];
261 "PRINT" 'L', SAMELINE, SCALED(9), I,'S5', TC[I];
262 CHARLIE:
263 "FOR" J:=1 "STEP" 1 "UNTIL" NC "DO" "BEGIN"
264 "READ" G[J,I];
265 "PRINT" SAMELINE,SCALED(9),'S5',J,'S3',I,'S3',G[J,I];
266 G[J,I]:=G[J,I]/AO[J];
267 "PRINT" 'S',SAMELINE,SCALED(9),G[J,I];
268 "END";
269 "END";
270 YORK:
271 "FOR" W:=1 "STEP" 1 "UNTIL" NC "DO" "BEGIN"
272 "PRINT" 'L5'ANALYSIS OF DATA FOR CELL=',SAMELINE,SCALED(9),W;
273 K1[W]:=K1G[W];
274 "PRINT" 'L'GUESSED K1=',SAMELINE,SCALED(9),K1[W];
275 K2[W]:=K2G[W];
276 "PRINT" 'L'GUESSED K2=',SAMELINE,SCALED(9),K2[W];
277 EBCW]:=EBG[W];
278 "FOR" I:=1"STEP"1"UNTIL"K"DO"
279 "BEGIN"
280 PC[I]:=GCW,I];
281 "PRINT" 'L',SAMELINE,SCALED(9),I,'S2',
282 TC[I],'S2',PC[I];
283 "END";
284 "PRINT" 'L'CYCLE STARTED**NUMBER=',SAMELINE,SCALED(9),W;
285 "FOR"V:=1"STEP"1"UNTIL"50"DO""BEGIN"

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```

286 "PRINT"'"L2\CYCLE NUMBER=' ,SAMELINE,SCALED(9),V;
287 R:=(K1[W]-K2[W])/K1[W];
288 EXB:=EB[W];
289 "IF"R>0.01"THEN"MXSET;
290 "IF"R<0.01"THEN"MXSETUP;
291 MXMAKE;
292 "PRINT"'"L\MXSETUP','L';
293 MXCOPY(B,A,3);
294 "PRINT"'"L\MATRIX A','L';
295 PRINTMX(A,3);
296 "PRINT"'"L\MATRIX B','L';
297 INVWX(B,3);
298 MXPROD(C,A,B,3);
299 PRINTMX(B,3);
300 "PRINT"'"L\MATRIX C','L';
301 PRINTMX(C,3);
302 COLUMN;
303 DK1[W]:=SA*B[1,1]+SB*B[1,2]+SC*B[1,3];
304 DK2[W]:=SA*B[2,1]+SB*B[2,2]+SC*B[2,3];
305 DEB[W]:=SA*B[3,1]+SB*B[3,2]+SC*B[3,3];
306 VV:=W;
307 K1[W]:=K1[W]+DK1[W];
308 K2[W]:=K2[W]+DK2[W];
309 EB[W]:=EB[W]+DEB[W];
310 "PRINT"'"L\CYCLE NUMBER =',SAMELINE,SCALED(9),V;
311 "PRINT"'"L\ESTIMATED K1=',SAMELINE,SCALED(9),K1[VV];
312 "PRINT"'"L\ESTIMATED K2=',SAMELINE,SCALED(9),K2[VV];
313 "PRINT"'"L\EST EXT COEF OF B=',SAMELINE,SCALED(9),EB[VV];
314 "IF"V=50"THEN""BEGIN"
315 "PRINT"'"L\50 CYCLES 50 OUT';
316 "GOTO" PETER;"END";
317 "IF" K1[W]<0 "THEN" "GOTO" IAN;
318 "IF" K2[W]<0 "THEN" "GOTO" IAN;
319 "IF" ABS(DK1[W]*100/K1[W])<0.01 "THEN" "GOTO" PETER;
320 IAN;
321 "END";PETER;
322 "PRINT"'"L\ANALYSIS COMPLETE';
323 "PRINT"'"L\CALCULATED K1=',SAMELINE,SCALED(9),K1[W];
324 "PRINT"'"L\CALCULATED K2=',SAMELINE,SCALED(9),K2[W];
325 "PRINT"'"L\CALCULATED EXB=',SAMELINE,SCALED(9),EB[W];
326 "COMMENT"NOW CALCULATE STANDARD ERRORS;
327 QD:=0;
328 "FOR" I:=1"STEP"1"UNTIL"K"DO""BEGIN"
329 "IF" T[I]=0"THEN""GOTO"LEEDS;
330 QD:=QD+((DELTAD[I])+2);
331 LEEDS: "END";
332 SEK1:=SQRT(ABS((R[1,1]*QD)/(K-3)));
333 SEK2:=SQRT(ABS((R[2,2]*QD)/(K-3)));
334 SEEB:=SQRT(ABS((R[3,3]*QD)/(K-3)));
335 "PRINT"'"L3\STANDARD ERROR OF K1=',SAMELINE,SCALED(9),SEK1
336 "PRINT"'"L3\STANDARD ERROR OF K2=',SAMELINE,SCALED(9),SEK2
337 "PRINT"'"L3\STANDARD ERROR OF EB=',SAMELINE,SCALED(9),SEEB
338 "END";
339 "PRINT"'"L\CHANGE';
340 "END";
770 NC
3132 CODE
3902 TOTAL

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APPENDICES REFERENCES

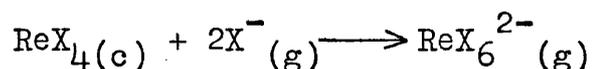
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SUMMARY

This thesis is concerned with aspects of the solution kinetics and thermochemistry of several binary and complex halides of rhenium.

The standard enthalpies of formation of potassium hexachlororhenate(IV), potassium hexabromorhenate(IV), β -rhenium tetrachloride, rhenium tetrabromide and rhenium oxide tetrachloride have been determined as -1333.1 ± 5.5 , -1036.0 ± 10.3 , -360.7 ± 15.1 , -303.0 ± 17.2 and -600.1 ± 16.6 kJ mol⁻¹, respectively. Hence, the Lewis acidities, ΔH_{2X^-} , of β -rhenium tetrachloride and rhenium tetrabromide have been estimated as -7.1 and $+135.4$ kJ mol⁻¹, respectively. ΔH_{2X^-} is the enthalpy change for the reaction,



The solution enthalpies of the sparingly soluble caesium hexachlororhenate(IV) and caesium hexabromorhenate(IV) have been determined as $+88$ and $+96$ kJ mol⁻¹, respectively. Hence, the single-ion hydration enthalpies of the gaseous hexachlororhenate(IV) and hexabromorhenate(IV) anions have been estimated as -846 and -784 kJ mol⁻¹, respectively, and have been compared with estimates for other polyatomic anions. Attempts have been made to correlate the solubility of caesium hexachlororhenate(IV) in mixed aqueous solvents with empirical solvent parameters and to estimate transfer parameters for the hexachlororhenate(IV) anion.

Metal-ion (Hg^{2+} , Tl^{3+} , Cd^{2+} and In^{3+}) catalysed reactions of hexachlororhenate(IV) and hexabromorhenate(IV) in acid aqueous solutions have been investigated. A rate law, rate constants and activation parameters have been determined and have been compared with data for similar systems. The possible connection between the effectiveness of the catalysts and the stability constants of their monohalo-complexes has been discussed.

The reactions of rhenium pentacarbonyl iodide, bromide and chloride with cyanide ion in methanol-water mixtures all follow a two step consecutive pattern, with the formation of a common product, $[\text{Re}(\text{CO})_4(\text{CN})_2]^-$. Rate laws, rate constants and activation parameters have been determined. The Gibbs free energy of transfer of rhenium pentacarbonyl iodide, from 50 vol.% to 70 vol.% methanol-water, has been estimated as -3.3 kJ mol^{-1} . The reactivity trend for the $\text{Re}(\text{CO})_5\text{I}/\text{CN}^-$ reaction upon change of solvent medium has been discussed in terms of transfer parameters.