



REDOX REACTIONS OF HALOGEN RADICAL
ANIONS WITH TRANSITION METAL CATIONS

by

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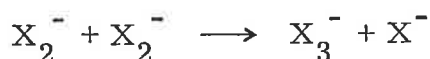
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SUMMARY

Halogen radical anions have been proposed as intermediates in many inorganic redox reactions involving halide ions or halogens. This thesis presents a detailed study of the reactions of halogen radical anions Cl_2^- , Br_2^- and I_2^- with divalent first row transition metal aquo-ions from vanadium through zinc.

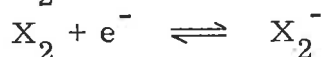
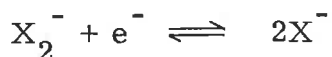
Flash photolysis and pulse radiolysis have been used to produce the radical anions (X_2^-). Rates and activation parameters have been obtained for their disproportionation reactions,



and reactions with aquated electrons and hydrogen atoms have been investigated. The equilibrium constants K_1 and K_2 for reactions leading to the formation of Cl_2^- from hydroxyl radicals (OH) have been measured.



E^0 values for the half reactions



have been calculated from available equilibrium and thermodynamic data. The resulting free energy changes have been verified by comparison with kinetic data.

Inorganic redox mechanisms can be classified as either inner or outer sphere. Inner-sphere mechanisms may be further defined as "substitution controlled" or "electron-transfer controlled". The large variation in $-\Delta G^0$ from 290 kJ mol^{-1} for $\text{Cr}^{2+}_{\text{aq}} + \text{Cl}_2^-$ to 21 kJ mol^{-1} for $\text{Mn}^{2+}_{\text{aq}} + \text{Br}_2^-$, and in ligand exchange rate from $\sim 8 \times 10^9 \text{ sec}^{-1}$ on $\text{Cr}^{2+}_{\text{aq}}$ to $\sim 10^2 \text{ sec}^{-1}$ on $\text{V}^{2+}_{\text{aq}}$ give rise to a variety of mechanisms. Product analysis, stoichiometries, rates, and activation parameters have been used to place the reactions

(ii)

studied into one of the above three categories. Variations in mechanism and kinetic parameters from metal to metal are discussed in terms of current theories of electron transfer processes. The results allow a critical assessment of reaction schemes proposing halogen radical anions as intermediates.

This thesis contains no material previously submitted for a degree or diploma in any University, and to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text.

A. THORNTON

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An acknowledgement would not be complete without thanking my parents for putting up with me for over twenty years and especially Ann Heylen for her continued friendship and help with the production of diagrams.

FOREWORD

The subject of this thesis involves the fields of free radical or radiation chemistry, and inorganic reaction kinetics. For this reason the discussion has been divided into two parts, Part I dealing with halogen radical anions, their production and properties, and Part II, which is to some extent dependent on Part I, dealing with the redox reactions of the radical anions with divalent first row transition metal aquo ions. The experimental techniques required for each study are similar and are covered mainly in Part I, however each part requires its own particular background knowledge and separate introductions have been written.

Experimental results which were not considered crucial to the discussion of results in Sections 4, 5, and 13 have been moved to the back of the thesis in Sections R4, R5 and R13 respectively. It is hoped that the important discussion sections will be more fluent because of the removal of this information which should be considered as supplementary.

PART I

PRODUCTION OF HALOGEN RADICAL ANIONS



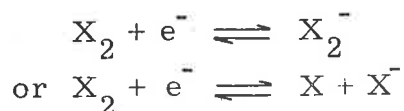
SECTION 1 - INTRODUCTION

1.1 HISTORICAL

The upsurge in the study of reaction kinetics in the 1920's led to the postulation of radical species in aqueous solution. Their importance in explaining many chain reactions and in particular photochemical processes was quickly realized. The existence of hydroxyl (OH) and hydroperoxy (HO₂) radicals was proposed, mainly in investigations on the catalyzed decomposition of hydrogen peroxide (Uri, 1952). Subsequently it was generally in vogue to break all mechanism down to one electron steps, necessitating the use of many radical species as intermediates in the reactions of two electron redox agents such as hydrogen peroxide, halogens, persulphates, oxygen and ozone.

1.1.1 Halogen radicals proposed as intermediates.

The recognition of halogens as accepting one electron at a time (Ardon & Plane, 1959) implies the existence of halogen atoms or radical anions in the reactions of halogens.



In the study of the reactions of ferric and ferricyanide ions with iodide ions, Wagner (1924) found a retarding effect of free iodide. This he attributed to a complexation of iodine atoms with iodide ion.



Dickinson & Ravitz (1930), Hershey & Bray (1936), and Fudge & Sykes (1952) later supported this proposition. The halogen radical anions were assumed to be quite stable with respect to halogen atoms and the speed of complexation was very high. As more reactions involving halogen atoms were studied it was realized that this retarding effect was more general. In the study of the photochemical reaction of halogens with hydrogen peroxide or oxalate,

Berthoud & Bellenot (1924) proposed Br_2^- . This was supported by Allmand & Young (1931) who also included I_2^- and later by Griffith, McKeown & Winn (1933 a, b) and Callow, Griffith & McKeown (1939).

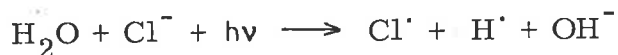


Taube & Bray (1940) were the first to propose Cl_2^- in the study of the retarding effect of excess chloride on the catalyzed chain reaction of ozone and hydrogen peroxide.



Between 1940 and the first direct observation of halogen radical anions in solution in 1955, several more workers proposed them as intermediates in the oxidation of halide ions by ferric and ceric ions (King & Pandow, 1953) or the photoreduction of halogens by manganous ions (Rutenberg & Taube, 1950; Rutenberg & Taube, 1951).

Meanwhile, various investigators had studied the photochemistry of halide ions. In 1931, Franck & Haber were the first to postulate that ultraviolet light produced chlorine atoms and hydrogen atoms from aqueous chloride solutions.



The calculations of Rabinowitch (1942) supported this hypothesis, suggesting that the adsorption bands of halide ions were in fact electron transfer to solvent in nature. The 1950's saw a revival in inorganic photochemistry. Rutenberg & Taube (1950, 1951), Roy, Hamill & Williams (1955) and Stottlemeyer (1954) proposed that halogen atoms or radical anions were formed in the photolysis of solutions of halogens.

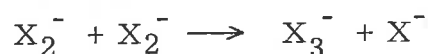


Rich & Taube (1954) also suggested the production of Cl_2^- from a transition metal complex PtCl_6^{2-} .

1.1.2 Direct observation of halogen radical anions.

Although unassigned until 1955, the first observation of halogen radical anions was made in 1896 when Goldstein reported that under the influence of ionizing radiation, alkali halide crystals assumed characteristic colours. The nature of these colour centres was the subject of much investigation (Seitz; 1946, 1954) until, using the new technique of ESR, Kanzig (1955) and Castner & Kanzig (1957) showed that the V centres in X-irradiated KCl crystals were due to the chlorine radical anion (Cl_2^-).

1955 saw the first real breakthrough in the study of the radical anions. With the newly developed technique of flash photolysis, Grossweiner & Matheson (1955) photolyzed halide ions and produced transients absorbing in the near UV. On the basis of the spectra it was proposed that they were the halogen radical anions (X_2^-). The observations were extended in 1957 by Grossweiner & Matheson when they reported the first directly observed reactions of the radical anions, the disproportionation reaction.



The development of pulse radiolysis proved to be of great importance to the study of the radical anions because as Taube & Bray (1940) had proposed, hydroxyl radicals, formed by irradiation, were found to react with halide ions to produce halogen atoms and subsequently the radical anions.

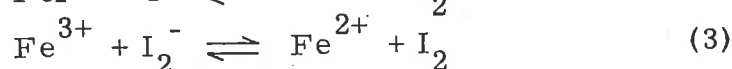
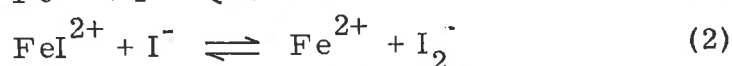
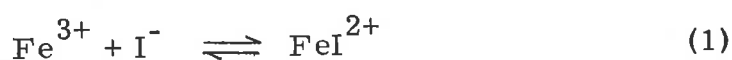


Many of the fundamental properties of the radicals have been investigated by pulse radiolysis.

1.2 CHEMICAL PRODUCTION OF HALOGEN RADICAL ANIONS

Strong oxidising agents can oxidise halide ions to halogens supposedly through the corresponding radical anion. Some properties of the radical anions can then be inferred from a detailed

study of the reaction mechanism. For example Fudge & Sykes (1952 a, b) proposed that the iodine radical anion formed in the oxidation of iodide ion by ferric ion reacted both with ferrous and ferric ions, the ratio of the constants, $k_2 : k_3$, being approximately 7:1

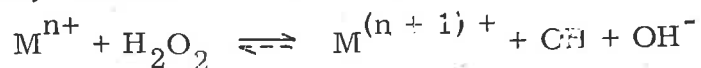


It is highly likely that reducing agents capable of reducing halogens to halide ions must also produce halogen radical anions as intermediates but studies on this type of system have in general been less detailed than studies on oxidation of halides. (e. g. Carter & Davidson, 1952; Conocchioli, Hamilton & Sutin, 1965; Malin & Swinehart, 1969). The use of these methods to study halogen radical anions, because they are indirect, is obviously limited and none but the most qualitative observations can be made.

Other radical species may be sufficiently powerful redox agents to convert halide ions or halogens to halogen radical anions. A particularly important example is the hydroxyl radical which oxidises halide ions to the radical anions, according to the stoichiometric equation.



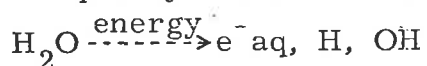
The details and importance of this reaction will be discussed in section 1.3. Chemical systems capable of producing hydroxyl radicals have been known for many years (Uri, 1952). Fenton type reagents in which a mixture of an oxidisable metal ion and hydrogen peroxide produce hydroxyl radicals have been used with success in many flow systems (e. g. Czapski & Samuni, 1969; Czapski, Levanon and Samuni, 1969).



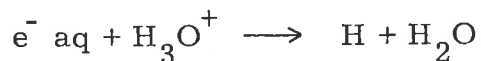
Addition of halide ion to such a solution should produce halogen radical anions, but complications due to the presence of the metal ion will undoubtedly be experienced. No such study has been reported.

1.3 RADIATION CHEMICAL PRODUCTION OF HALOGEN RADICAL ANIONS

High energy radiation causes the decomposition of water. The mechanism of this decomposition was the subject of much controversy until the advent of pulsed radiation sources in about 1960. The currently accepted theory is based on the radical mechanism developed by Weiss (1944).



The reducing species formed are aquated electrons (e^-_{aq}) and hydrogen atoms (H) which are interconverted according to the equation



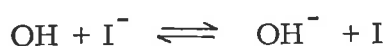
The major oxidising species is the hydroxyl radical (OH) and as Taube & Bray (1940) suggested, this species reacts with halide ions to produce halogen radical anions.



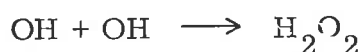
Section 4 of this thesis deals with primary and secondary radiation chemical processes in some detail. Section 11.5 gives some examples of redox reactions of the primary radiation chemical radicals. Only a brief resume of some studies on the radiation chemistry of halide solutions, to illustrate the importance of radiation chemistry to the study of halogen radical anions, will be given here.

In 1935 Fricke & Hart found that halide ions in moderate concentration produced a catalyzed decomposition of water under irradiation. At high iodide concentrations some iodine was formed.

Lanning & Lind (1938) confirmed this by producing iodine from irradiated aqueous solutions of hydrogen iodide and hydrogen iodide from irradiated aqueous solutions of iodine. Weiss (1944) interpreted Lanning & Lind's results in terms of the reaction of hydroxyl radicals with iodide.



In the 1950's the availability of ^{60}Co as a convenient source of penetrating γ radiation led to a resurgence in radiation chemistry and several workers found additional evidence for the reaction of hydroxyl radicals with halide ions by studying the effect of halide ions on the yield of hydrogen peroxide in aqueous solution (e. g. Sworski 1954, 1955a)



Pulsed electron irradiation in the 1960's allowed direct study of the reaction of hydroxyl radicals with halide ions and some reactions of halogen radical anions. The first report was in 1964 by Cercek Ebert, Keene & Swallow who produced Br_2^- from bromide solutions. Anbar & Thomas (1964) produced Cl_2^- from chloride solutions and Thomas (1965) reported the formation of I_2^- . Since 1965 radiation chemical techniques, in particular pulse radiolysis, have been used to establish many important properties of halogen radical anions.

1.4 PHOTOCHEMICAL PRODUCTION OF HALOGEN RADICAL ANIONS

In many instances it is possible to produce halogen atoms or radical anions by photochemical methods. Flash photolysis has proved particularly useful in studying halogen radical anions. It is convenient to distinguish systems in which halogen radicals are produced directly as a result of the primary photochemical act, from those in which the halogen radicals are produced indirectly by

secondary reactions of other radicals which are themselves produced photochemically. Systems which produce halogen radicals directly are discussed in terms of the nature of the primary photochemical reaction.[#]

1.4.1 Charge transfer to solvent. (CTTS)

In aqueous solution halide ions exhibit an intense adsorption around 200nm. Franck and Scheibe (1935) designated these spectra as "electron affinity" spectra. Rabinowitch (1942) interpreted the doublets observed in the I^-_{aq} and (less obviously) Br^-_{aq} spectra as due to the formation of halogen atoms in two states, $^2P_{3/2}$ and $^2P_{1/2}$, by a charge transfer process. The energy differences between the adsorption maxima of the two peaks in the doublet corresponded with those observed in the gas phase spectra of halogen atoms.

[#] Footnote

"Halogen radicals" is used as a collective term for halogen atoms (X) and halogen radical anions (X_2^-). Halogen atoms do not exhibit an accessible absorption spectrum but the radical anions are readily observed in the region 350-400 nm. They are rapidly interconverted according to the equilibrium.



The equilibrium constants are around 10^5 l mol^{-1} so that with free halide concentrations in excess of $10^{-5} \text{ mol l}^{-1}$, halogen radical anions will be the predominant species. The rate of approach to equilibrium is very fast so that unless observations can be made on a nanosecond time scale it is impossible to distinguish between primary processes producing halogen atoms or halogen radical anions. No such measurement has yet been made.

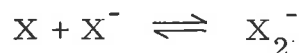
The nature of the species produced by the electron from the anion after the absorption was less clear. Studies of the effects of ionic strength and temperature and of the spectra of halide ions in non-aqueous solvents indicated that the fate of the electron excited by the charge-transfer absorption was dominated by the nature of the solvent. Stein & Treinin (1959, 1960) have proposed a model which predicts both the energies of the absorption peaks and the solvent and environmental effects with reasonable accuracy. The primary excited state is seen as an electron moving in an orbital involving the first hydration layer, but still centred on the parent atom.



Scavenger experiments show that this excited state does not react directly with added scavenger or with the solvent, but dissociates to form aquated electrons and halogen atoms in the bulk of the solution.



In the presence of excess halide equilibrium between halogen atoms and halogen radical anions is rapidly established.



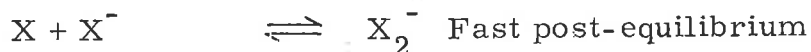
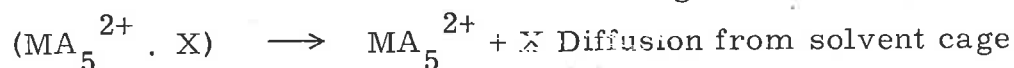
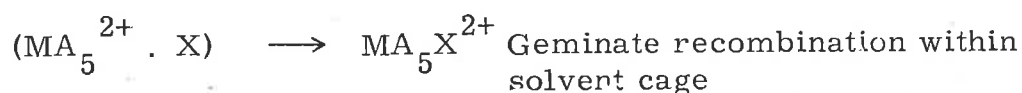
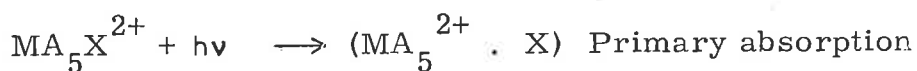
Flash photolysis studies have since confirmed the nature of the primary photochemical process. Grossweiner & Matheson (1957) have observed halogen radical anions, and Matheson, Mulac & Rabani (1963) observed the aquated electron in flash photolysed halide solutions. A comprehensive list of systems of this type in which halogen radical anions have been observed or proposed is given in table 1.4.

1.4.2 Charge transfer to metal.

(a) Inert complexes

Halogenopentaamminecobalt (III) complex cations exhibit a characteristic absorption band of high intensity in the ultra violet.

Because of its high intensity this band is attributed to a charge-transfer rather than a symmetry forbidden ligand-field excitation. The energy of the band maximum decreases from $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ (λ_{max} 228 nm) to $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ (λ_{max} 253 nm) to $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$ (λ_{max} 287 nm). This parallels the fall in electron affinity of the halogen atom of the complex. Linhard and Weigel (1951) were the first to propose in the 366 nm photolysis of $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$ that the absorption caused charge transfer to take place from ligand to metal (LMCT). Ligand to metal charge transfer is now well established as a process responsible for the photochemical reduction of transition metal complexes and flash photolysis of a series of halogenopentaamminecobalt (III) and rhodium (III) complexes has been shown to produce halogen radical anions (see table 1.4).



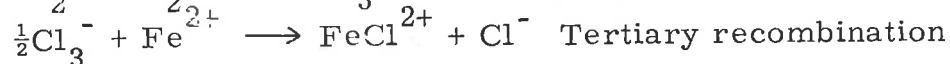
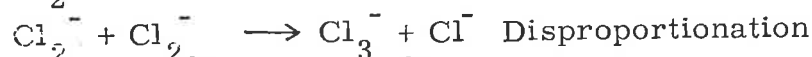
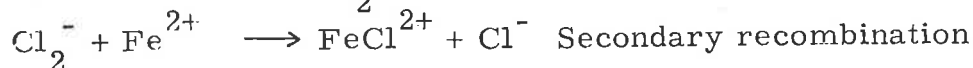
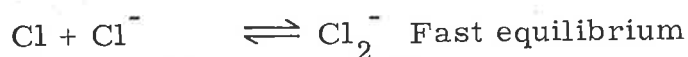
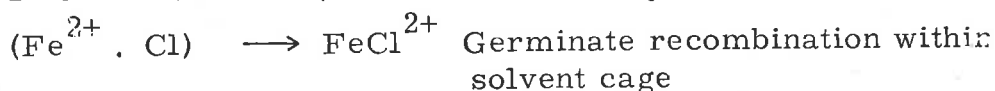
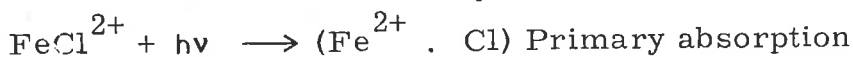
Ligand to metal charge transfer processes can occur in labile as well as inert transition metal complexes.

(b) Labile complexes

Despite the complication of dealing with equilibrium mixtures of various complexes, the charge transfer photochemistry of labile systems was investigated before inert systems. Fromherz & Lih (1931) analyzed the spectra of dilute solutions of lead halides in terms of superimposed absorption bands of Pb^{2+}aq and PbX^+aq . Fromherz & Walls (1936) obtained spectra of tetrahalogenotin (II) complex anions, and Rabinowitch & Stockmayer (1942) systematically

surveyed the spectra of halogenoiron (III) complexes. In these cases it was found that the difference in λ_{max} for the chloro-, bromo-, and iodo- complexes could be directly correlated with the electron affinity of the halogen atom (Rabinowitch, 1942), and the spectra were attributed to ligand to metal charge transfer excitations (LMCT).

Many labile complexes have low overall quantum yields due to secondary back reactions. Evans & Uri (1951) measured the quantum yield for production of chlorine atoms from monochloroiron (III) by scavenging the atoms (or radical anions) with vinyl monomers and measuring the polymer yields. The value of 0.13 at 300-400 nm that they obtained was very much greater than that obtained by measuring the concentrations of ferrous ion produced in the absence of scavengers, because the secondary back reactions are extremely efficient.



(c) Other complexes

Many other complexes (for example the halogeno-platinum group complexes) lie somewhere between the inert and labile complexes both in their substitution rates and their photochemical reactions. They also exhibit charge-transfer spectra that have been confidently assigned as LMCT spectra (Balzani & Carassiti, 1970). In some cases flash photolysis experiments have confirmed the formation of halogen radical anions (Wright & Laurence, 1972;

Langmuir & Hayon, 1967).

(d) Ion pairs

Oppositely charged ions can form outer-sphere complexes or ion pairs due to the electrostatic attraction between the ions. Ion pairs often show absorption bands in their spectrum which are not present in the spectra of the cation or anion alone (Linhard & Weigel, 1951). Photolysis in these bands generally leads to redox reactions. The classic example of a transition metal complex-halide ion pair, hexaamminecobalt (III)-iodide, has recently been shown to produce iodine radical anions when flash photolysed (Malone & Endicott, 1972)



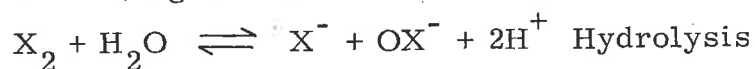
The primary photochemical process can be attributed to charge transfer from anion to cation (IPCT). The difference between this process and LMCT is that electron transfer must take place through ligands in the first coordination sphere of the metal ion.

The discussion of the photochemistry of transition metal complexes and ion pairs has been limited to systems in which halogen radical anions can be produced by photolysis. A more comprehensive list of photochemical systems of this kind in which halogen radical anions are formed is given in table 1.4. The photochemical reactions of metal complexes have been the subject of a number of recent reviews (Adamson, Waltz, Zinato, Watts, Fleischauer & Lindholm, 1968; Adamson, 1969; Endicott, 1970) of which that by Balzani & Carassiti (1970) is most comprehensive.

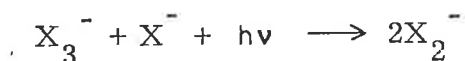
1.4.3 Direct bond dissociation/cleavage

In the gas phase in the visible region halogens exhibit a vibrational band spectrum which converges to a continuum due to

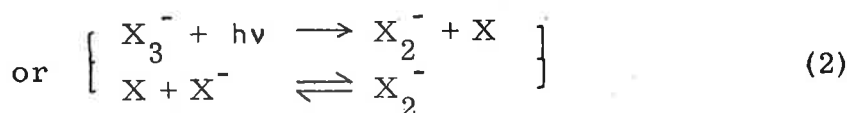
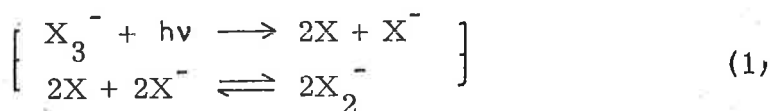
dissociation into atoms (Herzberg, 1966). Under very low pressures dissociation proceeds through an electronically excited state producing halogen atoms in the ground state ($^2P_{3/2}$) and excited state ($^2P_{1/2}$). At higher pressures and in solution, pre-dissociation from the upper state may be induced leading eventually to two ground state hydrogen atoms. Halogens are extensively hydrolysed in aqueous solution but by addition of excess halide ion and acid, hydrolysis can be suppressed and trihalide ions are formed. (Eigen & Kustin, 1962; Pink, 1970).



Trihalide ions exhibit intense absorption bands, $\lambda_{\max}$ decreasing from iodine (353 nm) to bromine (267 nm) to chlorine (220 nm). The energies of the absorption bands can be correlated with the gas phase spectra of halogens and with the bond strengths in the trihalide ions. Dissociation or bond cleavage (BC) takes place in the primary photolysis step. Halogen radical anions have been observed in the flash photolysis of trihalide ion solutions. (Stottlemeyer, 1953; Grossweiner & Matheson, 1957). The overall stoichiometric equation can be written.



The extreme lability of the (X_2^- , X) equilibrium precludes distinction between the two possible photolysis mechanisms (1) and (2), unless observations can be made on a sub-nanosecond time scale.



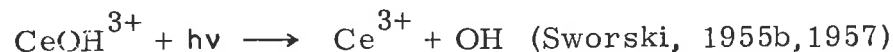
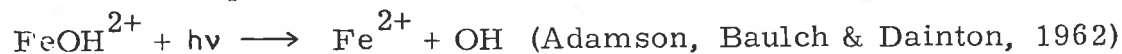
1.4.4 Production of X_2^- in a secondary photochemical reaction

Photolysis of hydroxide ion in aqueous solution produces hydroxyl radicals and aquated electrons. (Dainton & Fowles, 1965; Barrett, Fox & Mansell, 1966).



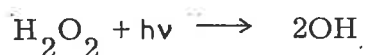
The usefulness of this reaction as a route to X_2^- production is limited by two complications. In alkaline conditions hydroxyl radicals do not react with chloride and react only slowly with bromide ion (see 4.4, 4.5), and λ_{max} for the hydroxide ion is at such short wavelengths (<190 nm) that very little effective light enters the solution.

Aqueous solutions of transition metal ions when photolysed often undergo charge transfer to metal type excitations (see 1.4.2). If the transfer is from a water molecule or hydroxide ion, hydroxyl radicals are produced.



The hydroxyl radicals can be scavenged by addition of halide ions. A system of this type will be suitable for study of the radical anions providing that the small concentrations of metal ions do not unduly interfere with the necessary measurements.

The simplest and best photochemical method for producing hydroxyl radicals is by bond cleavage or dissociation of hydrogen peroxide (Baxendale & Wilson, 1957).



The major complication in this system is that if the hydrogen peroxide concentration is too high or the scavenging rate too low, hydroxyl radicals may react with hydrogen peroxide (Fricke & Thomas, 1964; Thomas, 1965).

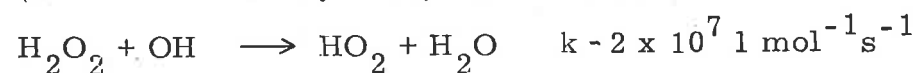


Table 1.4A

Photochemical Production of Halogen Radicals

Year	System	Process	X_2^-	Reference
1942	X^-	CTTS	Proposed	a
1957	X^-	CTTS	Observed	b
1963	X^-	CTTS	Observed	c
1972	X^-	CTTS	Observed	d
1959	Cl^-	CTTS	Observed	e
1965	Cl^-, Br^-	CTTS	Proposed	f
1967	Cl^-, Br^-	CTTS	Observed	g
1955	X_3^-	BC	Proposed	h
1950	Cl_2	BC	Proposed	i
1951	Br_2	BC	Proposed	j
1954	I_3^-	BC	Observed	k
1957	I_3^-	BC	Observed	b
1958	CoA_5X^{2+}	LMCT	Proposed	l
1958	CoA_5X^{2+}	LMCT	Proposed	m
1965	CoA_5X^{2+}	LMCT	Observed	n
1965	CoA_5X^{2+}	LMCT	Proposed	o
1972	CoA_5X^{2+}	LMCT	Observed	d
1963	CoA_5Br^{2+}	LMCT	Proposed	p
1970	CoA_5Br^{2+}	LMCT	Proposed	q
1970	CoA_5Br^{2+}	LMCT	Observed	r
1970	RhA_5I^{2+}	LMCT	Observed	s
1972	RhA_5I^{2+}	LMCT	Observed	t
1960	PtX_6^{2-}	LMCT	Proposed	u
1963	PtX_6^{2-}	LMCT	Proposed	p
1954	$PtCl_6^{2-}$	LMCT	Proposed	v
1972	$PtCl_6^{2-}$	LMCT	Observed	w

Year	System	Process	X_2^-	Reference
1970	$PtA_4X_2^{2+}$	LMCT	Proposed	x
1972	$PtA_4Br_2^{2+}$	LMCT	Observed	y
1967	HgX_4^{2-}	LMCT	Observed	g
1942	FeX^{2+}	LMCT	Proposed	a
1942	FeX^{2+}	LMCT	Proposed	z
1949	$FeCl^{2+}$	LMCT	Proposed	aa
1951	$FeCl^{2+}$	LMCT	Proposed	bb
1958	$CoA_6^{3+} \cdot X^-$	IPCT	Proposed	1
1972	$CoA_6^{3+} \cdot X^-$	IPCT	Observed	d

Notes (Table 1.4A)

X = Cl, Br and I

For an explanation of process see 1.4

References

- (a) Rabinowitch (1942)
- (b) Grossweiner & Matheson (1957)
- (c) Matheson, Mulac & Rabani (1963)
- (d) Malone & Endicott (1972)
- (e) Edgecombe & Norrish (1959)
- (f) Dainton & Fowles (1965)
- (g) Langmuir & Hayon (1967)
- (h) Roy, Hamill & Williams (1955)
- (i) Rutenberg & Taube (1950)
- (j) Rutenberg & Taube (1951)
- (k) Stottlemeyer (1953)
- (l) Adamson & Sporer (1953a)
- (m) Adamson & Sporer (1958b)
- (n) Penkett & Adamson (1965)
- (o) Endicott (1970)

- (p) Fleischauer (1963)
- (q) Endicott (1970)
- (r) Caspari, Hughes, Endicott & Hoffman (1970)
- (s) Kelly & Endicott (1970)
- (t) Kelly & Endicott (1972)
- (u) Adamson (1960)
- (v) Rich & Taube (1954)
- (w) Wright & Laurence (1972)
- (x) Moggi, Varani, Manfrin & Balzani (1970)
- (y) Fleischauer & Adamson
- (z) Uri (1952)
- (aa) Evans & Uri (1949)
- (bb) Evans, Santappa & Uri (1951)

1.5 PROPERTIES OF HALOGEN RADICAL ANIONS

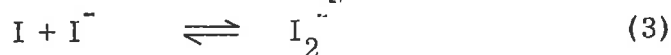
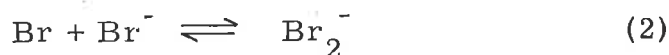
1.5.1 Equilibria and thermodynamic properties

When Grossweiner & Matheson (1955, 1957) first observed transient spectra in the flash photolysis of halide ions and halogens, they realized that the spectra in the near UV ($\lambda_{\text{max}} \sim 360 \text{ nm}$) could not be due to halogen atoms. Much earlier, several workers had found retarding effect of halide ions on reactions involving halogen atoms and attributed them to the formation of halogen radical anions (see 1.1.1)



Conclusive evidence was obtained that the species observed in irradiated alkali halide crystals was X_2^- rather than X atoms, by ESR when it was shown that the electron density was shared by exactly two halogen atoms (Kanzig, 1955).

More recently pulse radiolysis has confirmed this conclusion. The equilibrium constant for the formation of Br_2^- and I_2^- from the corresponding halogen atom has been determined by observing the dependence of the absorbance due to the radical anion upon the concentration of halide ion. The equilibrium constants for the reactions



are $(2.2 \pm 1) \times 10^5 \text{ l mol}^{-1}$ (Cercek, Ebert, Gilbert & Swallow, 1965) and $1.1 \times 10^5 \text{ l mol}^{-1}$ (Baxendale et al., 1968). Repetition of the I_2^- results at temperatures up to 80°C gave ΔH° for the equilibrium as -23 kJ mol^{-1} (Baxendale & Bevan, 1969). From the free energy change (ΔG°) one finds ΔS° is $+17 \text{ J mol}^{-1} \text{ K}^{-1}$. The small positive value implies that loss of solvent order around the large I_2^- ion outweighs the negative change to be expected upon complexation. The stability of I_2^- is almost totally due to enthalpy rather than entropy terms. For Br_2^- no temperature dependence

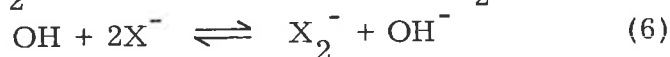
of the equilibrium constant has been reported. The equilibrium constant for Cl_2^- formation has not been previously measured but by analogy with the other halogens is assumed to be around 10^5 l mol^{-1} . (Malone & Endicott, 1972), in agreement with our currently measured value. (see 4.5).

The rate of attainment of equilibrium between X and X_2^- is very rapid, probably diffusion controlled. Early work on the Br_2^- system showed that k_2 was greater than $5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ (Cercek et al., 1965; Sutton et al., 1965). In 1966, Matheson, Mulac, Weeks & Rabani estimated it as $\sim 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$, a conclusion supported by later investigations (Zehavi & Rabani, 1972). The rate of formation of I_2^- from the hydroxyl radicals has been shown to be limited by the value of k_3 ; Baxendale, Bevan & Stott (1968) obtained $k_3 = 7.6 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

The extreme lability of this equilibrium means that despite the unfavourable value of the equilibrium constant, if a substrate reacts much faster ($> 10^4$ times) with X than with X_2^- reaction through the free halogen atom may be important. Sutton, Adams, Boag & Michael (1965) proposed that the reaction of Br_2^- with hydrogen peroxide occurs only through bromine atoms.

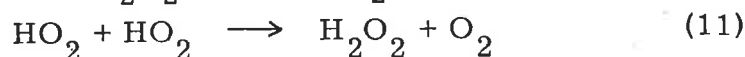
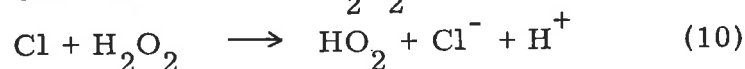
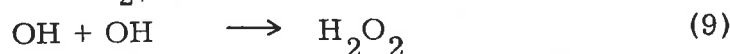
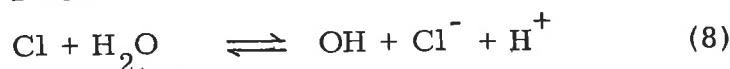
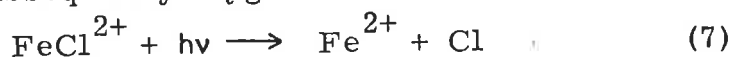


At low acid concentrations the equilibrium (6) between OH and Cl_2^- (and to a lesser extent Br_2^-) may lie towards the left.



As before, the rapidity of the reactions allows Cl_2^- to react through hydroxyl radicals. This was qualitatively recognized in the photolysis of chloroiron (III) complexes at $\text{pH} > 2$ where oxygen is evolved (Buxton, Wilford & Williams, 1962). It is proposed that chlorine atoms formed in the primary

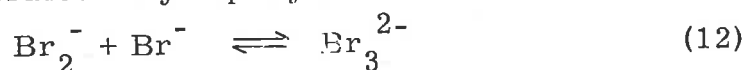
photolysis step react with water to produce hydroxyl radicals and subsequently oxygen.



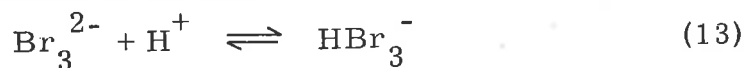
With $\text{pH} > 2$ and chloride concentrations $< 0.05 \text{ mol l}^{-1}$

K_6 is such that equilibrium (6) lies well to the right. (see 4.5)

In more concentrated solutions of halide ion, there is evidence that higher complexes than X_2^- may be formed. In 1972, Cercek observed spectra in 0.3 mol l^{-1} NaBr that he attributed to the tribromide radical anion Br_3^{2-} . This species was formed very rapidly.



The equilibrium constant, K_{12} , is given as 20 l mol^{-1} but the measurement relies upon small differences in extinction coefficient at 270 nm, a wavelength where interference by tribromide ion ($\lambda_{\text{max}} = 267 \text{ nm}$, $\epsilon = 4 \times 10^4$) would be severe. According to Cercek the tribromide radical anion has a pK_a of 3.7, the result again depending on measurements of small differences at 270 nm.



More extensive investigations of equilibria in solutions of high halide concentration are required to confirm these results.

1.5.2 Spectra of halogen radical anions

The electronic absorption spectra of the halogen radical anions were first reported by Grossweiner & Matheson (1957). Their spectra have proved essentially accurate despite improvement in experimental techniques. The three spectra are shown in Fig. 1.5. The only difference from the spectra of Grossweiner

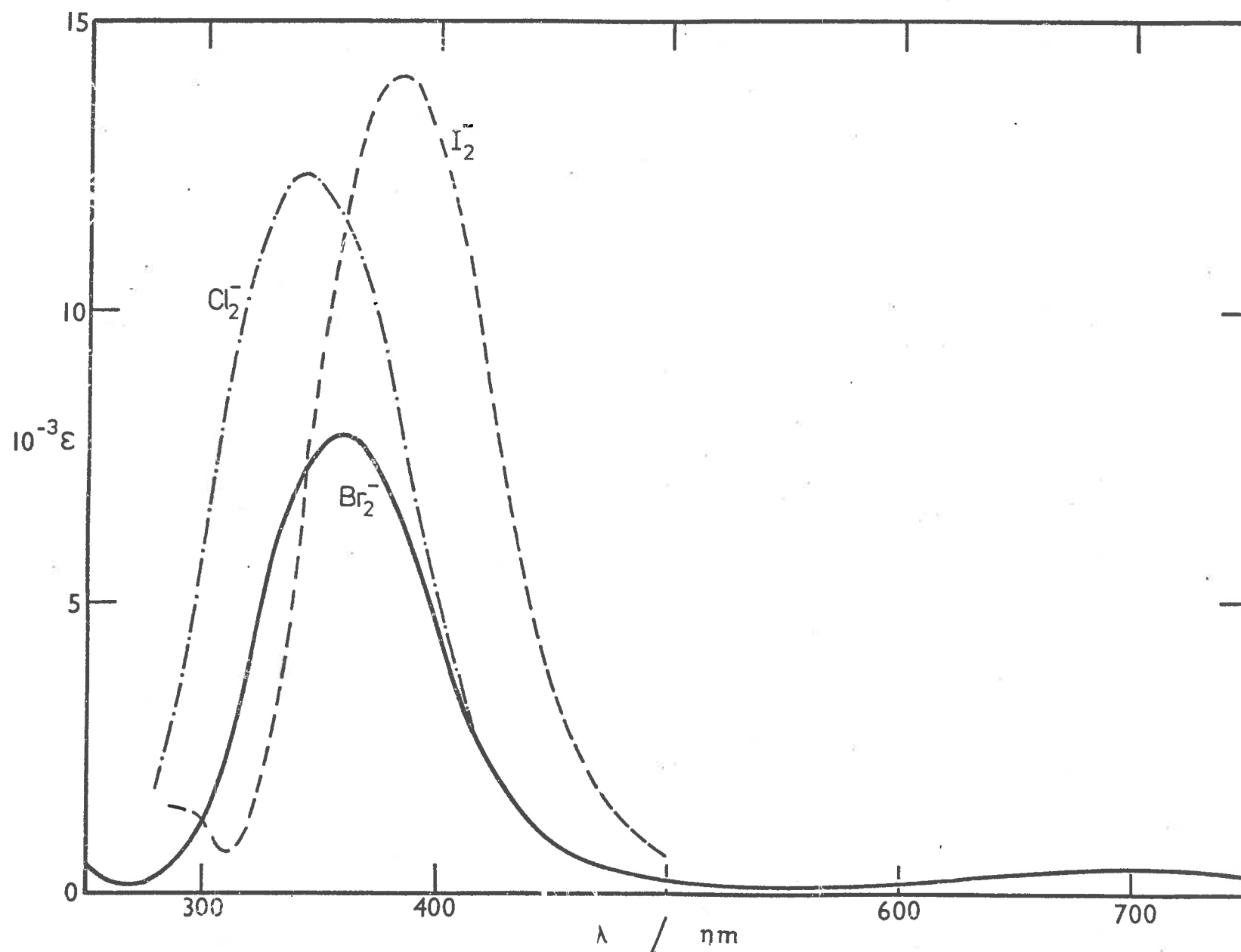


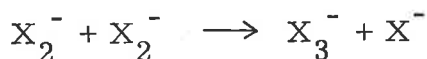
Fig. 1.5 . Spectra of Halogen Radical Anions

& Matheson is the appearance of another lower intensity band at 700 nm for Br_2^- , reported by Zehavi & Rabani (1972). The extinction coefficients at maxima are large for all three species (see Fig. 1.5), making detection of the radical anions in micromolar quantities a relatively easy matter. The spectra in the solid state, either in crystals or glasses, show good agreement with those in the liquid phase (Brown & Dainton, 1966).

ESR spectra have been measured in alkali halide crystals (Kanzig, 1955) and in glasses at 77°K (Brown & Dainton, 1966; Marov & Symons, 1971). The spectra have been assigned to halogen radical anions as they show electron density shared between two identical halogen atoms.

1.5.3 Reactions of halogen radical anions

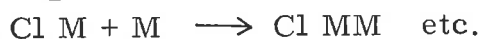
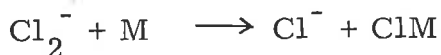
Halogen radical anions show both radical and redox properties. As radicals they dimerize (disproportionate)



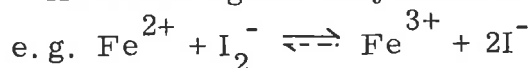
react with other radicals



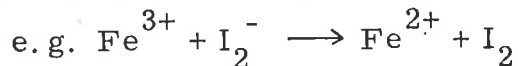
and initiate radical polymerization (Evans & Uri, 1949).



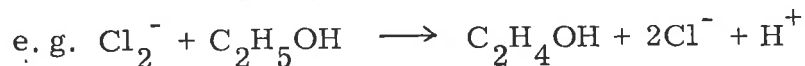
As redox agents they oxidise metal ions



reduce metal ions (Fudge & Sykes, 1952)



and react with many organic compounds (Langmuir & Hayon, 1967)



Part 1 of this thesis generally deals with radical properties of halogen radical anions and reactions of Br_2^- , Cl_2^- and I_2^- are covered in sections 5.3, 5.4 and 5.5. respectively.

Part 2 deals with redox reactions of halogen radical anions and transition metal ions. Section 11.6 contains a table of the standard reduction potentials of halogen radical anions and summarises previous redox studies.

SECTION 2 - EXPERIMENTAL

2.1 APPARATUS - GENERAL DESCRIPTION

2.1.1 Flash photolysis

The experimental arrangement for flash photolysis is shown diagrammatically in Fig. 2.1A.

The photolysis flash is produced by discharge of an energy storage capacitor through a xenon-oxygen filled flash lamp. Discharge is triggered by an ignitron-thyratron circuit which simultaneously produces a pulse to trigger the oscilloscope time-base. Should a second oscilloscope trace be desirable, an adjustable-delay pulse generator is incorporated in the trigger circuit.

Changes in the solutions being studied are monitored spectrophotometrically by a xenon or xenon-mercury lamp. The emergent beam passes into a monochromator-photomultiplier system. The signal from the photomultiplier is reduced in impedance by a voltage follower and displayed as a function of time on a storage oscilloscope.

Relevant specifications, layout, and circuit details are given in Appendix 1.

2.1.2 Pulse radiolysis

The experimental arrangement for pulse radiolysis is shown diagrammatically in Fig. 2.1B.

The system is similar to that used in flash photolysis except that the light flash is replaced by an electron pulse of about 2 μ sec duration delivered from a 1.3 MeV Van der Graaf accelerator. The electrons enter the cell in a direction perpendicular to the monitoring beam.

The system used at the Australian Atomic Energy Commission, Lucas Heights, has been previously described. (Bullock & Cooper, 1970)

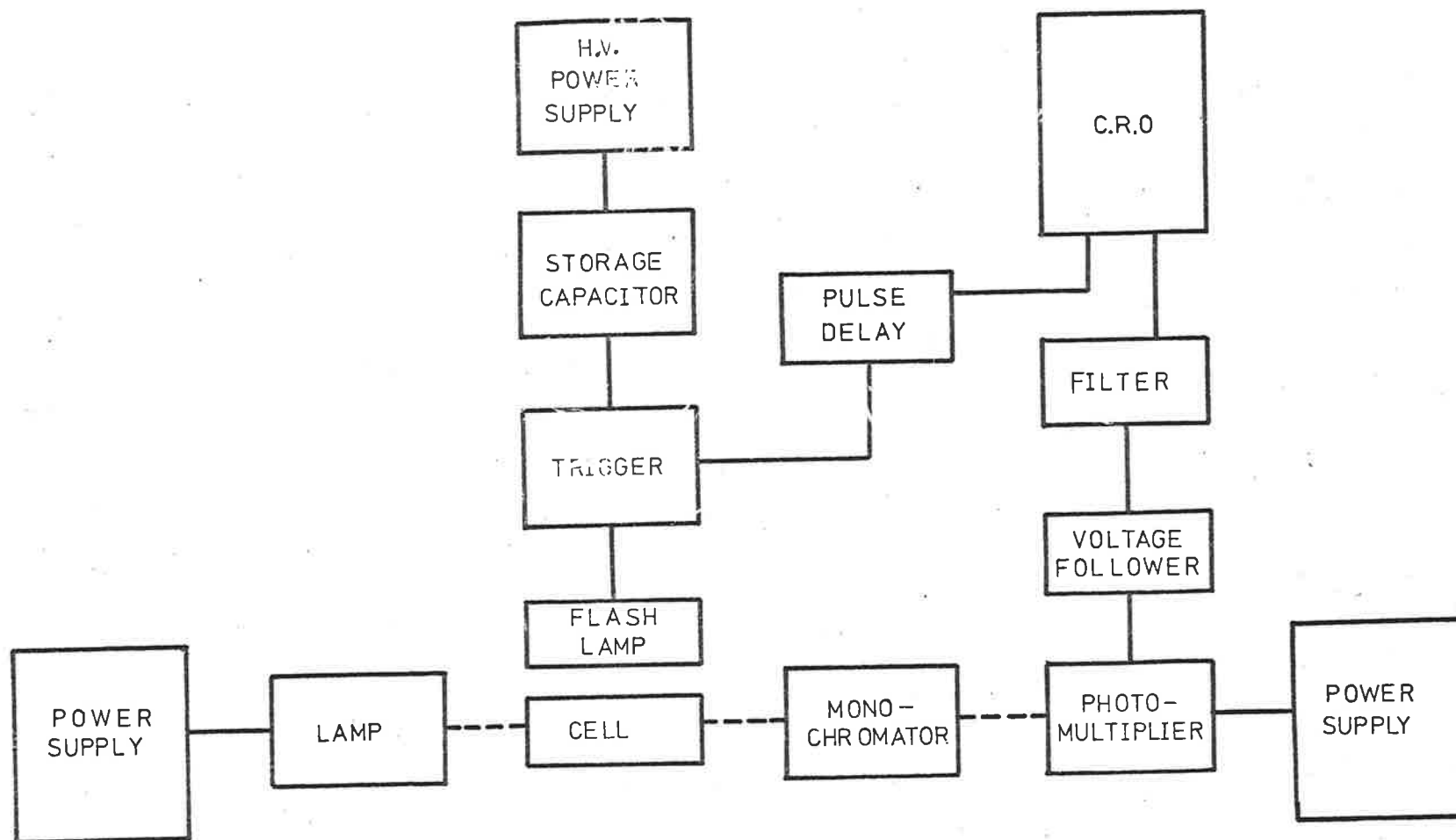


Fig. 2.1A Experimental Arrangement - Flash Photolysis

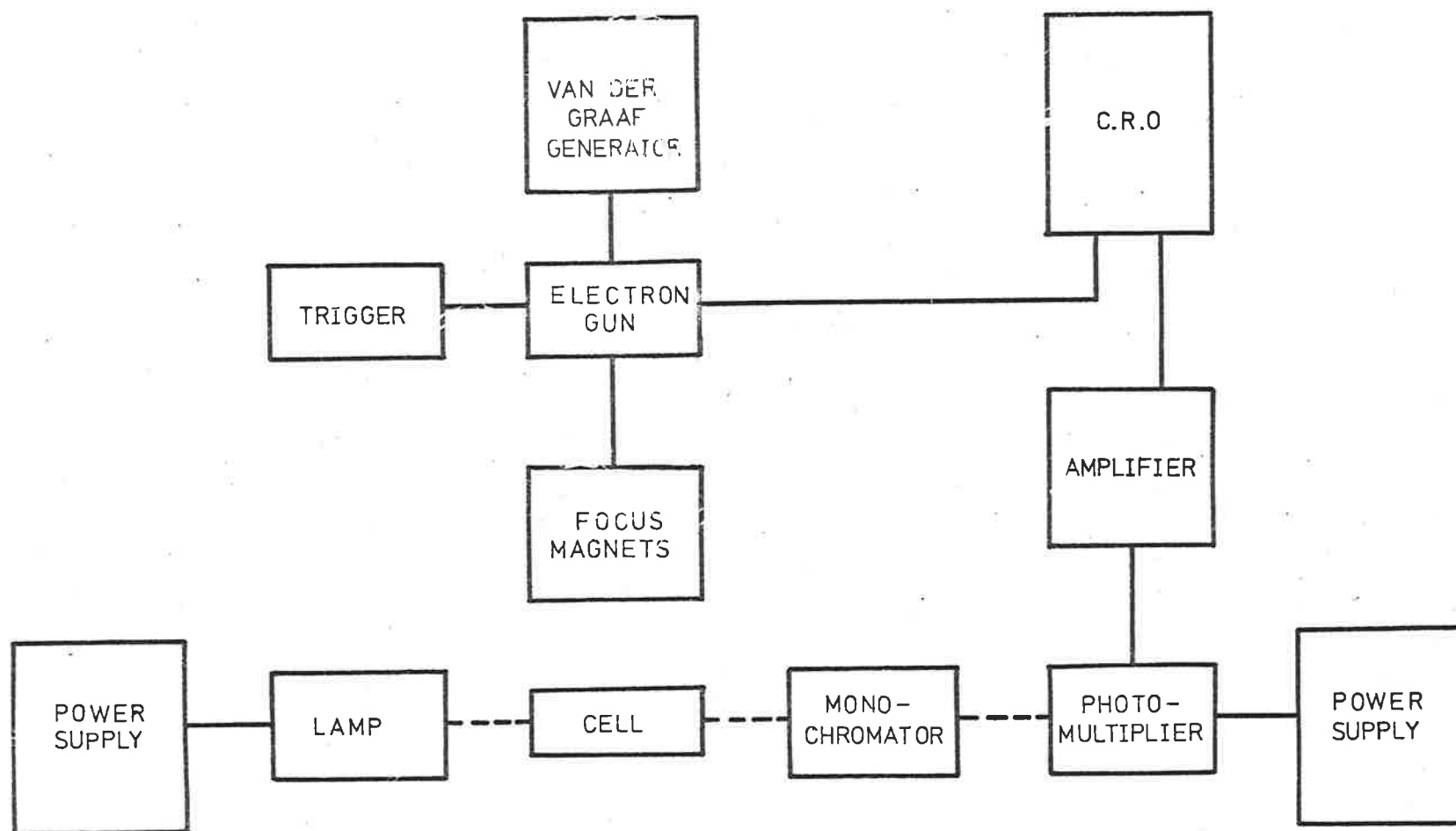


Fig. 2.1B Experimental Arrangement - Pulse Radiolysis

2.2 PERFORMANCE - FLASH PHOTOLYSIS

The suitability of the flash photolysis apparatus for a particular study may be limited by several factors, e.g. the resolution time, the noise associated with the detection system, the reproducibility or power of the photolysis flash etc. In section 2.2 the major limitations are considered individually.

2.2.1 Flash lamp

During the discharge of the flash lamp observation of reactions is difficult because transients are still being formed and stray light from the flash may interfere with the monitoring light signal (see 2.2.2). Optimum conditions require minimum discharge time and maximum energy output.

Fig. 2.2A shows a typical intensity vs time plot for the light flash. The rise time or time taken to reach maximum intensity was $8\ \mu\text{s}$ and the half width of the flash at half height was $4\ \mu\text{s}$. Approximately 500 J were dissipated per flash. The spectral distribution of the light from the flash lamp was not measured but there is no reason to suspect that it differs substantially from that obtained by other workers using inert-gas filled discharge lamps. Christie & Porter (1952) found that the spectral distribution in the region 240-440 nm is independent of :

- (a) inert gas used
- (b) filling pressure (provided it is greater than 5cm of Hg)
- (c) energy of discharge (provided it is greater than 500 J)

Combining their measurements with those of Edgerton (1946) the spectral distribution shown in Fig. 2.2B is obtained. The spectrum is a continuum within the measured range and although measurements were not made below 240 nm, it is evident from the fact that $1\ \mu\text{mol l}^{-1}$ concentrations of Cl_2^- can be produced

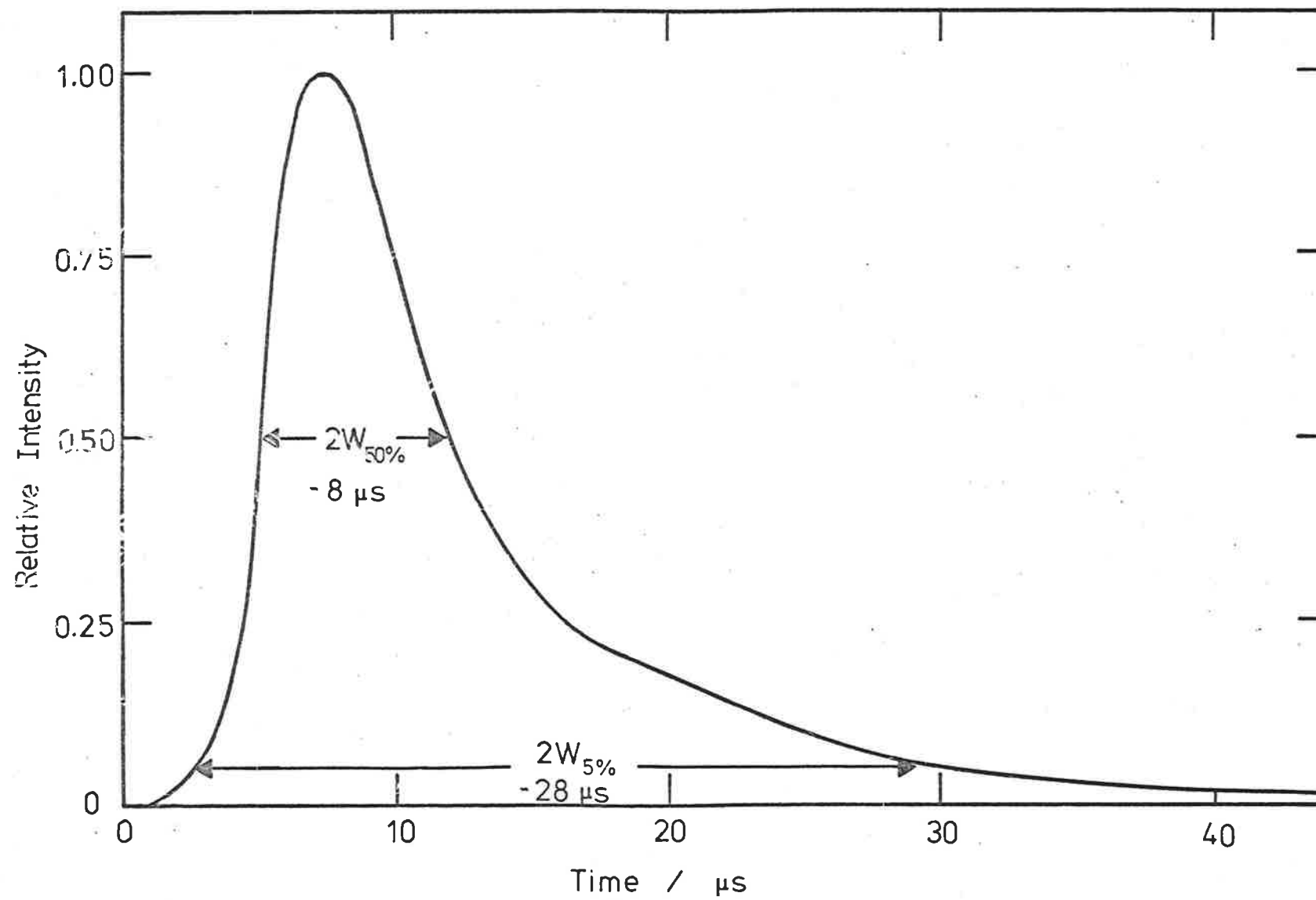


Fig. 2.2A Flash Profile

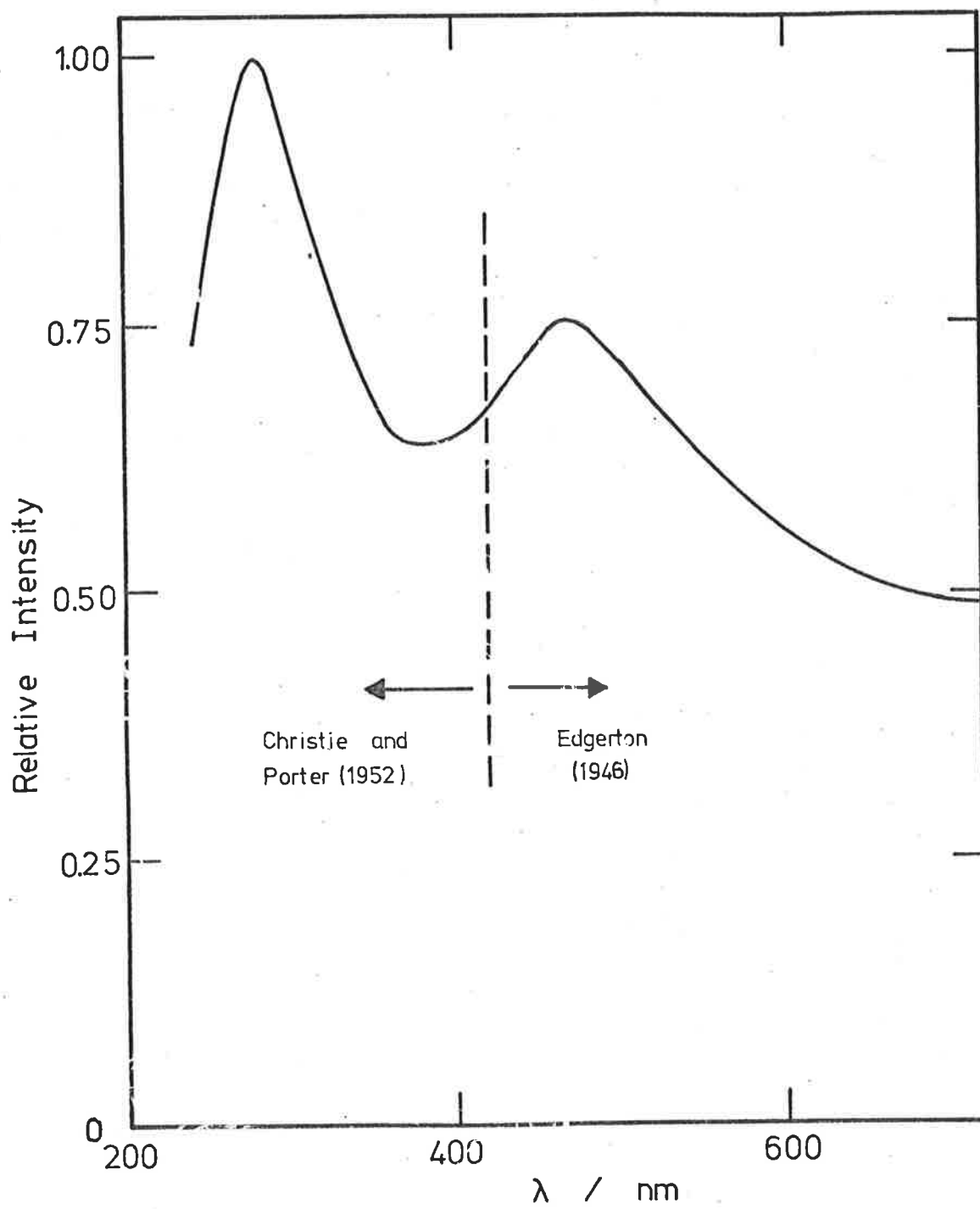


Fig. 2.2B Flash Spectral Distribution

from chloride solutions ($\lambda_{\text{max}} \sim 190 \text{ nm}$), that the intensity at wavelengths below 240 nm is sufficient for our purpose.

2.2.2 Stray light from the flash

Interference by light from the flash on observation of the monitoring light signal depends on several factors, primarily the relative intensity of the monitoring beam and the stray light entering the monochromator. Consequently interference is most severe when observations are made at wavelengths less than 300 nm or on absorbing solutions, because in both cases the monitoring signal is considerably attenuated (relative to a non-absorbing solution at about 400 nm). Interference can be reduced by restricting observations to wavelengths where a mercury-xenon lamp gives out narrow high intensity lines (e.g. 297, 313, 366, 405 nm).

Interference can also be reduced, at the expense of some overall signal, by increasing the degree of collimation on the input slits of the monochromator. With the present 1 mm holes and a non absorbing solution, at a mercury line, the signal produced by stray light from the flash is less than 300 mV high and can if necessary be subtracted from the absorption signal which is typically 1 V in magnitude. In the worst instances where significant absorption by the solution takes place, observations may be restricted to times later than 50 μs . This is not an untenable restriction.

2.2.3 Electrical interference from flash

Careful attention to earth points was the main requirement to minimize electrical pickup. All components and power supplies were isolated from any large conductor (such as racks to hold power supplies or the aluminium alloy top of the apparatus) and earth wires were run to a single point. Total enclosure of

power supplies, especially for the voltage follower, was also important.

The limiting interference in the final arrangement was found to be pickup directly by the oscilloscope. The intensity was independent of attachment of signal cables to the scope, appeared unattenuated even if the inputs were shorted to earth, and was reduced as the distance between the oscilloscope and the discharge was increased. With the oscilloscope at 3 m distance the maximum observed trace deflection was about 2 mm. This was considered negligible compared to the likely signals to be measured. The duration of the pickup signal was of the same order as the light flash ($\sim 30 \mu\text{s}$), however it oscillated about zero with a frequency of about 5×10^4 Hertz.

2.2.4 Monitoring light

High frequency noise in the light signal from the xenon or mercury-xenon lamp is negligible. The power supply emits a small amount of 100 Hertz ripple. The signal to noise ratio is about 250 and except where extreme sensitivity is required this is negligible.

A more troublesome feature is instability in the arc position. The susceptibility of discharge lamps to this type of fluctuation is unpredictable and varies with the make of the lamp, the type (i. e. Xe or Xe-Hg), the age of the lamp and from lamp to lamp within a particular make. Generally it was found that compact arc 75W lamps were more stable than the larger 150W lamps. Various methods were tried to stabilize the arc such as application of magnetic fields. These efforts were of limited effectiveness; occasionally a lamp was temporarily stabilized. Measurements with a fluctuating arc were impossible, the signal to noise ratio was often less than 5 and the period of oscillation varied from 0.5 to 2 seconds. The only solution was

rejection of unstable lamps.

2.2.5 Detection system

Long term stability in the detection system is excellent. There is no 50 Hertz noise in the EHT supply of the photo multiplier. High frequency "shot" noise under conditions of low light intensity is the major limitation in the detection system. This can generally be avoided by observation at a wavelength of high monitoring light intensity. Noise can also arise if the components of the detection system are not rigidly clamped to the bench. A particularly troublesome example was an oscillation with a period of about 0.1 seconds detected after firing the lamp. The source of this noise was found to be a physical vibration of the monochromator collimator initiated by the shock of the discharge.

2.2.6 Response time

The major limitation on the rate of any reaction that can be studied is imposed by the duration of the photolysing flash (see 2.2.1). In most instances stray light (see 2.2.2) and electrical interference (see 2.2.3) limit observations to times later than 40 μs . If the half life of the reaction is less than 12 μs , then in 40 μs , even transients produced in 10 $\mu\text{mol l}^{-1}$ concentrations have decayed to a concentration of about 1 $\mu\text{mol l}^{-1}$. A reaction with a half life of 12 μs is in most instances the fastest that can be observed.

The response time of the detection system is limited by stray capacitance in the circuit. The half time for a signal to rise is about 0.5 μs whilst the fall half time is about 2 μs . When compared with the limitations imposed by the flash duration this is not normally a serious complication.

2.3 OBSERVED SIGNAL TO NOISE RATIOS - FLASH PHOTOLYSIS

The best way to illustrate errors likely to occur in

measurement of the halogen radical anion concentration as a function of time, given the likely limitations discussed in 2. 2, is to discuss the various systems used to generate halogen radical anions, separately. Chloride, bromide and iodide are not treated individually; it is generally found that within a factor of 2 the same yield of X_2^- is produced for each halogen. Consequently differences occurring in the overall signal to noise ratios are not usually large.

2. 3. 1 Flash photolysis of halide solutions

Solutions of halide ions generally produce about $1 \mu\text{mol l}^{-1}$ concentrations of radical anions when flashed. With an extinction coefficient of 10^4 and in a 10 cm cell this corresponds to an optical density of 0.1 or a change of 800 mV in a 4.0 V incident light signal. Observation at the intense 366 nm mercury line would give less than 10 mV high frequency noise. Coupled with about 15 mV of 100 Hertz ripple from the lamp this results in an overall signal to noise ratio of about 30 producing an excellent trace (for example see Fig. R5. 3A)

2. 3. 2 Flash photolysis of halogen solutions

About $6 \mu\text{mol l}^{-1}$ concentrations of radical anions can be produced from halogen solutions. This corresponds to an optical density of about 0.6 and voltage changes of 3V in a 4V incident signal. The improvement in signal to noise ratio (relative to halide solutions which produce only $1 \mu\text{mol l}^{-1}$ concentrations) that would be expected is somewhat offset by the necessity of using higher photomultiplier EHT's because the tri-iodide ion, I_3^- , and bromine, Br_2 , absorb significantly at 366 nm, cutting down the transmitted light signal. Nevertheless a signal to noise ratio of about 100 is usually obtained (for example see Fig. R5. 3H)

Most of the reactions of the radical anions were followed in halogen solution. If the reaction rate is fast ($t_{1/2} \sim 12 \mu\text{s}$) compared to the flash duration then significantly less than the initial $6 \mu\text{mol l}^{-1}$ concentration of halogen radical anions will be observed. (see 2.2.6). For an observed concentration of about $1 \mu\text{mol l}^{-1}$ the average signal to noise ratio is about 10 (for example see Fig. R13.3B).

2.3.3 Flash photolysis of halogenoiron (III) complexes

Flash photolysis of $\sim 10^{-4} \text{ mol l}^{-1}$ concentrations of bromo and chloroiron (III) complexes produces about $6 \mu\text{mol l}^{-1}$ concentrations of X_2^- . The extinction coefficients of FeCl^{2+} and FeBr^{2+} at 366 nm are about 1000 and 500 respectively and attenuation of the monitoring light signal is large. The average signal to noise ratio for observation of X_2^- in these solutions is about 40, but good traces are still obtained (for example see Fig. R5.3J)

2.3.4 Flash photolysis of hydrogen peroxide

Between 10 and $15 \mu\text{mol l}^{-1}$ concentrations of hydroxyl radicals were produced by the unfiltered flash from dilute ($10^{-3} - 10^{-2} \text{ mol l}^{-1}$) solutions of hydrogen peroxide. In the presence of acid, hydroxyl radicals are rapidly and quantitatively scavenged by halide ions to produce halogen radical anions (see 1.4.4) Hydrogen peroxide does not absorb significantly above 280 nm so that the monitoring beam is not significantly attenuated. The transmittance changes ($\sim 3.6 \text{ V}$ in 4 V incident light) show signal to noise ratios of about 200. Excellent traces are obtained. (For example see Fig. R5.3I)

2.4 PERFORMANCE - PULSE RADIOLYSIS

The experimental arrangement for pulse radiolysis is very similar to that for flash photolysis (see 2.1). Many of the

same limitations discussed in 2.2 apply here. The pulse radiolysis facility at Lucas Heights performs poorly by comparison with facilities in other laboratories (Matheson & Dorfman, 1969) but the major additions necessary to upgrade its performance are still under consideration. The performance figures quoted below are typical, not necessarily optimum.

2.4.1 Electron pulse

The electron pulse from the 1.3 MeV Van der Graaf acceleration is of about 2 μ sec duration with an average current of about 10 mA, which is critically dependent upon the state of the cathode. Between 500 2000 rads are delivered per pulse and the spread of the beam on the surface of the cell is about 1.7 cm². Fig. 2.4A shows a typical current vs time plot for a single pulse. Observations during the pulse are usually possible, subject to interference by Cherenkov radiation (see 2.4.2), but allowance for the rate of build-up of transients must be made.

The major problem experienced with the pulse is a lack of dose reproducibility. Variations of up to 20% are common with occasional pulses showing a 50% variation. For kinetic investigations these may not be serious but for equilibrium constant determinations (e. g. see 4.5) these fluctuations, particularly in the long term, are a serious problem.

2.4.2 Cherenkov radiation

Absorption of high energy radiation by a transparent medium results in the emission of lower energy quanta. This effect produces a light flash of the same duration as the electron pulse and a spectral distribution showing increasing intensity at shorter wavelengths. ($I \propto \lambda^{-2}$; Franck & Tamm, 1937). The emission is predominantly in a broad cone in the forward

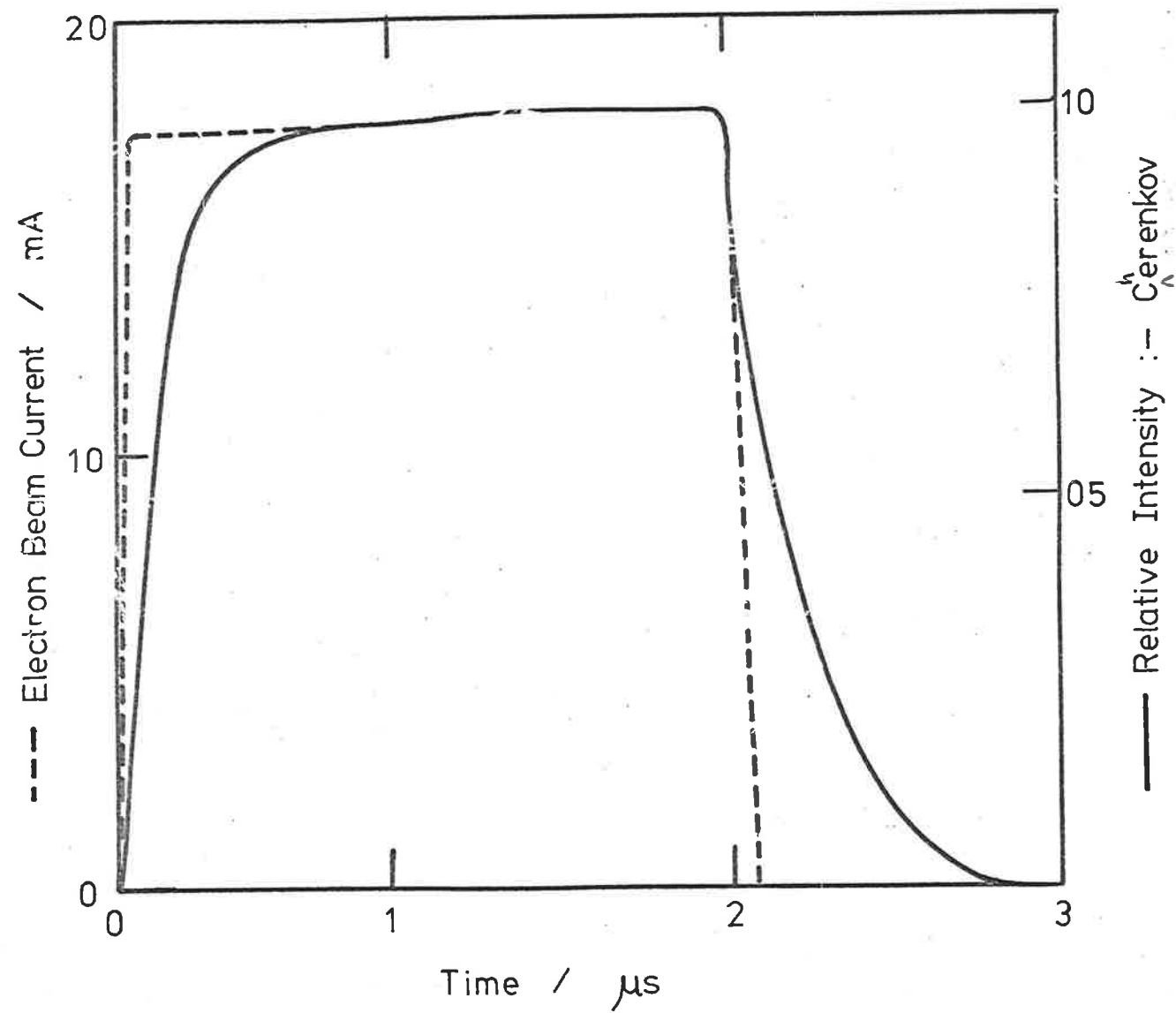


Fig. 2.4A Pulse profile

direction (Shaede & Walker, 1969) so that the usual normality of monitoring beam and electron beam minimizes the amount of Cerenkov entering the monochromator-photomultiplier system. At wavelengths below 400 nm the amount of Cerenkov radiation scattered into the monochromator may be significant. Fortunately its duration is only equal to that of the pulse and unless the detection system is driven beyond a point where it can readily return to its equilibrium condition, observations can be made immediately after the pulse. Should observations during the pulse be necessary allowance for the effect of Cerenkov radiation can be made provided it is not too severe.

2.4.3 Electrical interference from electron pulse

To shield the operator from xrays produced in the pulse the apparatus, with the exception of the oscilloscope and power supplies, is contained in a heavily shielded room. This shielding also minimizes the electrical interference caused by the electron pulse, the only sensitive components remaining in close proximity to the pulse being the photomultiplier and its associated amplifier. These are contained in metal cases and the shielding appears quite adequate; no electrical interference from the pulse could be detected.

2.4.4 Monitoring light

The light source used in the existing pulse radiolysis set is a 300 W xenon lamp. This type of lamp requires considerably more complex power supplies than the ones used for flash photolysis (see 2.2.4) but the particular lamps used in this work showed good arc stability. The noise level on the light signal was negligible compared with the noise introduced by the detection system. (see 2.4.5)

2.4.5 Detection system

The detection system is similar to that used in flash

photolysis except that an AC amplifier is used in place of the voltage follower (cf 2.2.5). High frequency noise in both the photomultiplier EHT supply and the amplifier results in considerable high frequency noise in the signal. Typical signal to noise ratios of about 100 are observed for the unattenuated monitoring light signal in the region 300 - 600 nm.

2.4.6. Response time

As in flash photolysis the major limitation on the maximum reaction rate that can conveniently be studied is imposed by the duration of the pulse. A 2 μ s pulse requires a half life in excess of 2 μ s for convenient observation and imposes an absolute lower limit of about 1 μ s on the half life of any reaction that can be studied.

The response time of the detection system can be seen in the rounding of the $\overset{h}{C}erenkov$ radiation signal (see Fig. 2.4A). With an infinitely short response time the $\overset{h}{C}erenkov$ radiation should be the same square shape as the pulse. The apparent half time for rise and fall of the $\overset{h}{C}erenkov$ signal is 0.5 μ s which does not cause any distortion in signals decaying with half lives of 2 μ s or more.

2.5 OBSERVED SIGNAL TO NOISE RATIO - PULSE RADIOLYSIS

The yield of radicals produced in pulse radiolysis depends primarily on the dose rate. With the exception of solutions that contain certain scavengers capable of doubling the yield of one radical, at the expense of another, (see 4.3) the yield is independent of the nature of the solution. Observation of halogen radical anions is made at about 350 nm, a wavelength at which the response of the detection system is close to optimum. Other transients may not absorb so strongly or may absorb at less convenient wavelengths, in which case the observed

signal to noise ratios will be correspondingly higher.

A 1000 rad dose produces about $2.5 \mu\text{mol l}^{-1}$ concentrations of halogen radical anions from halide solutions. In a 1 cm cell with an extinction coefficient of 10^4 this corresponds to an optical density of 0.025 and an observed signal of about 200 mV with an incident light intensity of 4V. The signal to noise ratio in this instance is about 5, but under favourable conditions where both the dose and the yield of halogen radical anions can be increased signal to noise ratios of up to 20 can be obtained.

2.6 REAGENTS AND STANDARDIZATION

Only reagents used in the production of halogen radical anions and investigation of their subsequent decay are discussed in 2.6. Redox reactions and the necessary reagents are covered in Part II of the thesis (for reagents see section 12.1).

2.6.1 Reagents

Sodium chloride and sodium bromide were BDH or May and Baker Anala R grade. Potassium iodide used was Univa R brand. Where ionic strength was adjusted, Fluka puriss sodium perchlorate was used.

BDH Anala R iodine and bromine were used to make up halogen solutions. Chlorine was prepared by the action of concentrated hydrochloric acid on Anala R potassium permanganate. It was once vacuum distilled and stored in a bulb on a vacuum line. Dilute aqueous solutions were prepared by distilling quantities into frozen aqueous solutions. Hydrogen peroxide was obtained as a stabilizer free 30% solution from Laporte chemicals.

To adjust acidities G. F. Smith Anala R perchloric acid was used. All water was deionized and then double distilled

from neutral permanganate and acidic dichromate under an atmosphere of oxygen in an all glass still.

CIG high-purity dry nitrogen or dry argon was scrubbed in a chromous chloride scrubbing column to remove residual oxygen. Nitrous oxide was once vacuum distilled medical grade from CIG. Oxygen for solutions or to fill gas lamps was untreated CIG medical grade, whilst xenon was grade X, 99.999% obtained from British Oxygen.

All solutions were stored in stoppered glass vessels as preliminary results had shown that storage in polythene for an extended period was likely to affect the reproducibility of the results.

2.6.2 Standardization

Alkali halides were generally taken as primary standards. Where necessary standardization against silver nitrate was performed potentiometrically. Sodium perchlorate was estimated gravimetrically by drying aliquots at 110°C . Perchloric acid was standardized against Anala R sodium tetraborate and hydrogen peroxide by redox titration with potassium permanganate.

Halogens were usually estimated spectrophotometrically by conversion to the tri-halide ion with excess halide. Chlorine was converted to tri-iodide by reaction with excess iodide.

2.7 EXPERIMENTAL METHODS - FLASH PHOTOLYSIS

2.7.1 Aerated solutions

As will be shown later most reactions of halogen radical anions were unaffected by the presence of oxygen or air (see sections 5.3.7, 5.4.7). To study such a system it is necessary only to put it in a stoppered 10 cm quartz spectrophotometer cell through which the monitoring beam

passes, adjacent to the flash lamp.

2.7.2 Temperature controlled aerated solutions

To control temperature the 5 cm quartz jacketed cell shown in Fig. 2.7A is used. A peristaltic pump circulates thermostated deionized water through the jacket. The aerated solution is simply placed in the solution compartment of the cell.

Above 200 nm absorbance and scattering of the flash light by the water jacket is insignificantly greater than in a non-jacketed cell. The temperature which is monitored by a thermistor is controlled to $\pm 0.2^{\circ}\text{C}$. Temperature rises caused by a single flash are less than 0.1°C .

2.7.3 Deaerated solutions

In the study of some reactions of iodine radical anions it is necessary to remove oxygen from the solution. This is achieved in either of two ways.

(a) Evacuation method

The solution is placed in the bulb section of the cell shown in Fig. 2.7B. It is frozen in liquid nitrogen, pumped to a low pressure ($\sim 10\ \mu\text{m}$ of Hg) on a vacuum line and then thawed. The procedure is repeated at least once or until a good vacuum ($\sim 1\ \mu\text{m}$ of Hg) is obtained, and the solution tipped into the cell side of the apparatus.

(b) Replacement method

If another gas such as nitrogen or argon is bubbled through an aerated solution for a sufficiently long time displacement of the oxygen will take place. Intermittant evacuation of the atmosphere above the solution aids dissolution of the oxygen. The apparatus illustrated in Fig. 2.7C uses this method to remove oxygen from solutions in which solvent

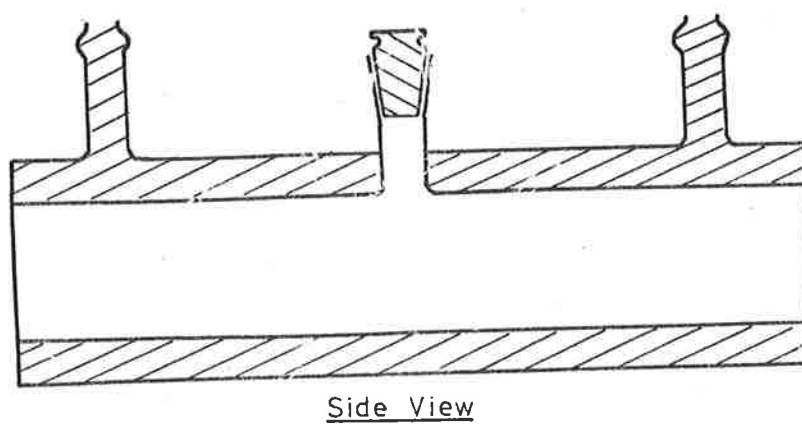
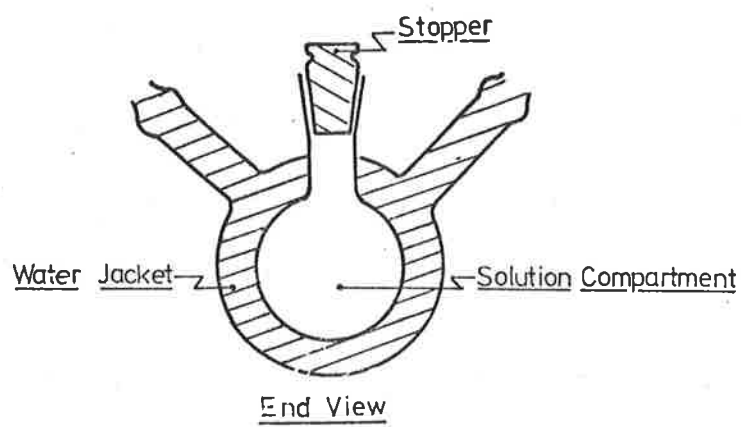


Fig. 2.7A Jacketed Quartz Cell

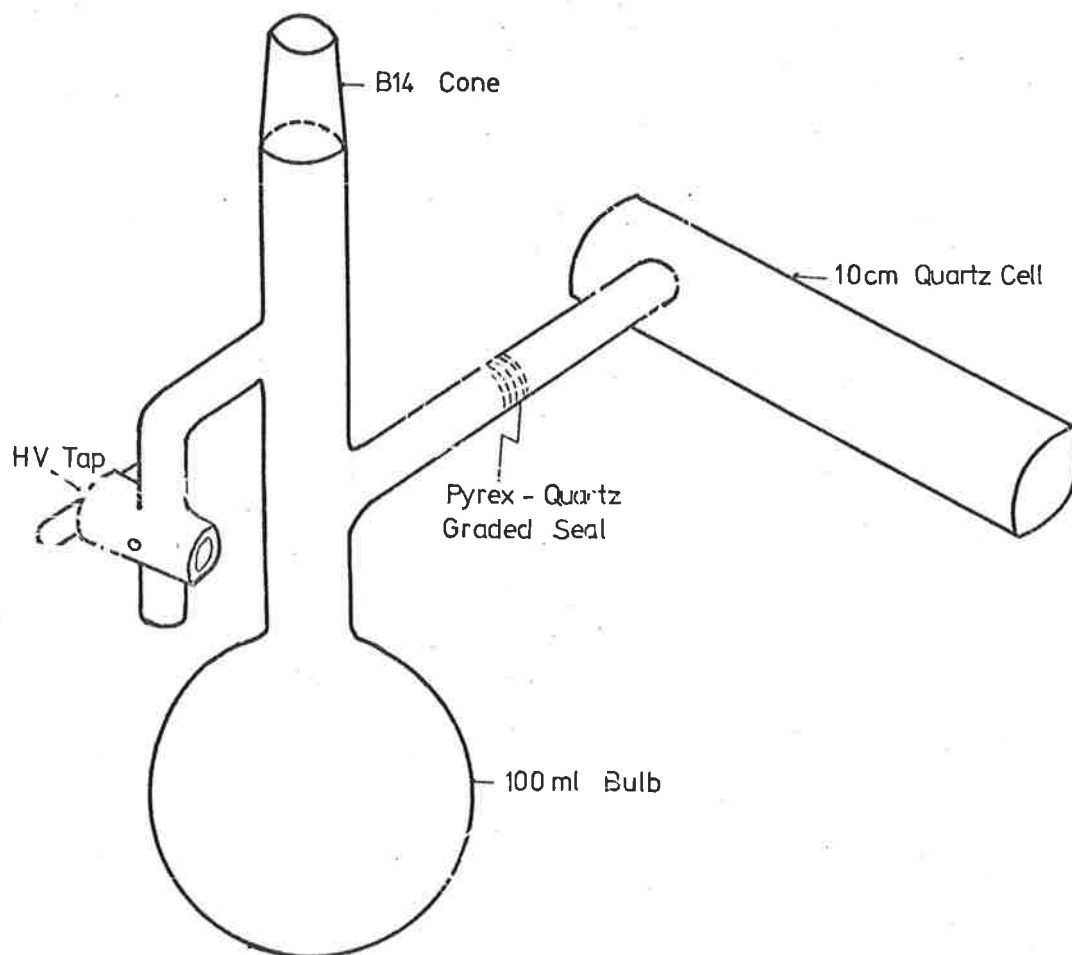


Fig. 2.7B Flash Photolysis Cell

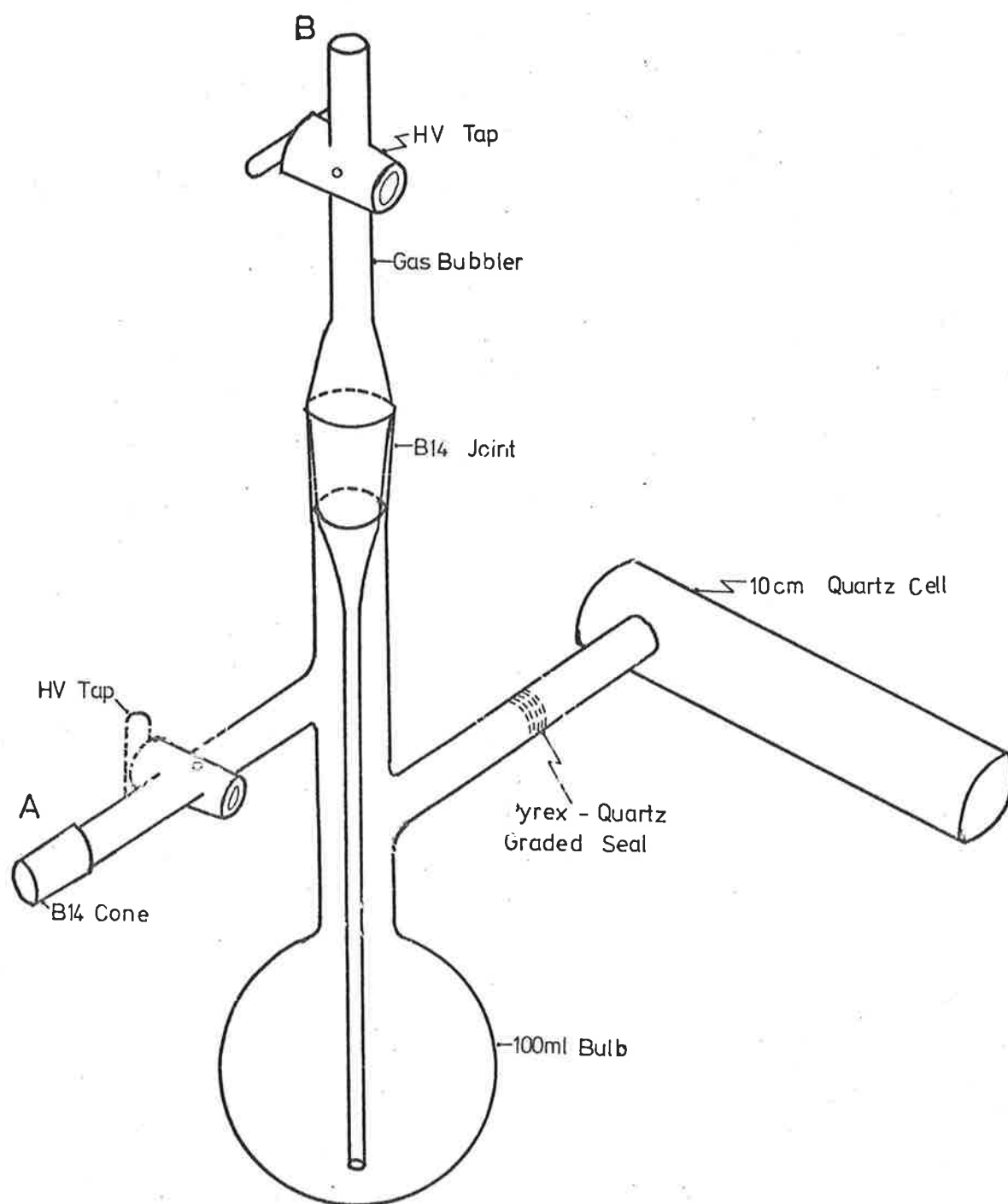


Fig. 2.7C Flash Photolysis Cell

loss is not critical. Up to 1 ml (in 50 ml) of water may be lost in the procedure.

The solution to be deoxygenated is placed in the bulb and evacuated through A. Nitrogen is then admitted through B and allowed to bubble through the solution for about 60 s. the procedure is usually repeated twice.

2.7.4 Gas saturated solutions

It is often necessary to saturate a solution with a particular gas such as oxygen or nitrous oxide. Two methods can again be used, their application depending upon the accuracy required in the final volume.

(a) Evacuation method

A teflon coated magnetic stirring bar is placed in the bulb of Fig. 2.7B prior to the addition of the solution. The deaeration procedure described in section 2.7.3 (a) is performed and the cell left on the vacuum line. After the final thawing the desired gas is introduced and the solution stirred for about 15 minutes to achieve saturation. The concentration of gas in the solution can be estimated from the pressure over the solution and its solubility. When it is necessary to vary the concentration of the gas this method must be used.

(b) Replacement method

When a small loss of solvent is unimportant the more convenient replacement method can be used. The procedure given in 2.7.3 (b) is repeated using the desired gas to replace the air from the solution. The final bubbling with gas is of extended duration (about 5 min.) to ensure saturation of the solution. The concentration of gas is assumed equal to its saturation solubility.

2.7.5 Temperature controlled deaerated solutions

The water jacketed cell has no provision for deaeration, however, by use of a syringe technique deaerated solutions can be used and air entry kept to a minimum. A rubber seal with a hole for the thermistor is inserted in place of the cell stopper, (see Fig. 2.7A). Nitrogen or other gas is passed into the cell through a syringe needle inserted through the seal. Another syringe needle is used to vent the nitrogen out of the cell. The solution to be used is deaerated by a replacement method and injected into the cell through the outlet syringe needle which is then removed. A small positive pressure of gas is applied to the solution throughout the experiment.

2.8 EXPERIMENTAL METHODS - PULSE RADIOLYSIS

2.8.1 Aerated solutions

The cell for use in pulse radiolysis is shown in Fig. 2.8A. The face through which the electron beam passes is ground down to minimum thickness to prevent attenuation of the electron beam. Observations are made as close as possible to this front face because 1.3 MeV electrons penetrate only about 3 mm in a medium of density 1.0.

The solution to be irradiated is placed in a syringe and subsequently injected through the two-way tap A into the cell. After irradiation the solution is ejected through A by application of gas pressure to the solution through B.

2.8.1 Deaerated solutions

Solutions to be deaerated are placed in a syringe and the plunger removed. The desired gas is then bubbled through the solution from the syringe outlet for about 10 minutes to replace air from the solution. The plunger is re-inserted and

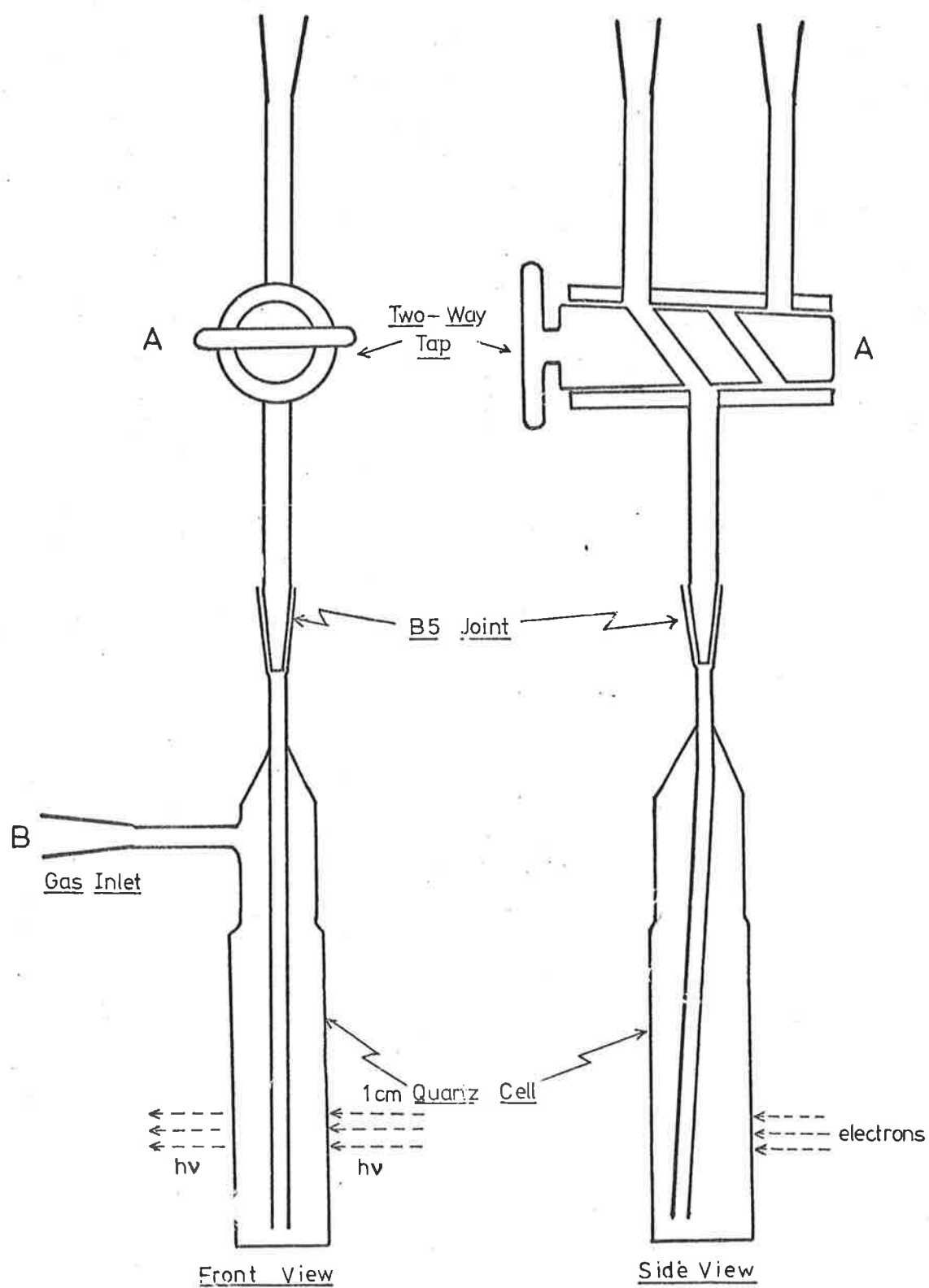


Fig. 2.8A Pulse Radiolysis Cell

37.

the syringe capped.

With nitrogen or other gas flowing into the cell through B and out through tap A, the syringe is placed on top of A and solution forced into the cell against the nitrogen pressure.

SECTION 3 - TREATMENT OF RESULTS

3.1 INTERPRETATION OF OSCILLOSCOPE TRACES

When a solution is subjected to a pulse of irradiation (light or electrons) changes in optical density due to formation of transients may occur. Consequently the intensity of the monitoring light signal entering the photomultiplier is attenuated and the photomultiplier output reflects this change. A trace of photomultiplier output against time is recorded on the oscilloscope. In many cases the percentage change in light signal is small and it is desirable to observe only changes in light signal by subtracting a constant voltage, equal to the observed voltage before pulsing, from the photomultiplier signal. This facility is provided by use of a voltage comparator amplifier in the oscilloscope.

3.2 MEASUREMENT OF OSCILLOSCOPE TRACES

The oscilloscope stores the signal on the screen. Voltage changes can be read directly from the screen to an accuracy of $\pm 2\%$ (for a 5 cm deflection). This is often sufficient for spectral measurements but not for kinetics. By photographing the trace onto 10 x 12 cm Polaroid 3000 or Kodak Tri-X pan film the photograph can be directly measured to about $\pm 1\%$ accuracy. Further improvement can be obtained by use of a manually driven trace reading machine (see Appendix 12) which displays a digital voltage proportional to the vertical displacement. Accuracy of $\pm 0.5\%$ can be achieved with this method. The most accurate but inconvenient method involves enlargement of the Tri-X pan transparency to an accurately known ($\sim 4\times$) magnification and manual copying onto graph paper. Use of thick ester based 10 x 12 cm transparencies minimizes distortion. Accuracy of $\pm 0.2\%$ is possible with this method.

3.3 CONVERSION TO OPTICAL DENSITIES

Prior to kinetic analysis the voltage vs time curve displayed on

the trace must be converted to an optical density vs time curve. Between 10 and 20 voltages are read at fixed times and these are converted by the following method.

At any time, t , the optical density relative to that before pulsing can be calculated from the expression,

$$OD_t = \log_{10} \frac{V_o}{V_t} = \log_{10} \frac{V_o}{V_o - \Delta V_t}$$

where V_o is the voltage observed before flashing

V_t is the voltage observed at time t

ΔV_t is the change in voltage observed at time t

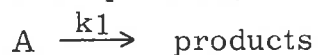
By adjusting the EHT applied to the photomultiplier its response can be adjusted to give a fixed initial output voltage, V_o (usually 4.0V). The repetitive nature of the calculation of OD can then be eliminated by preparing a computed tabulation of ΔV_t , at a fixed V_o , with corresponding OD_t and if desired, the simple integrated rate law expressions of $\log_e OD_t$ and $1/OD_t$. The program for preparing tables and a sample output is given in Appendix 4. 1.

Alternatively the entire calculation of rate constants (for simple systems) or optical densities can be computerized. Program A (see Appendix 4. 2) performs this function and must be used in preference to the tables where V_o is not fixed or is not a convenient number.

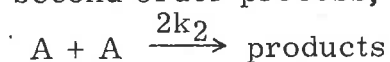
3.4 DERIVATION OF RATE CONSTANTS

3.4.1 Simple decay/formation kinetics

When the observed species A reacts by or is formed by a simple first order process,



or a simple second order process,

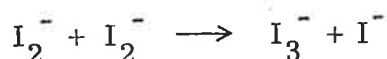


the integrated rate expressions $\log_e [A]_t$ and $1/[A]_t$ when plotted against time give straight lines of slope equal to the rate constant, k , or k_2 . When A is the only absorbing species at the wavelength of

of observation plots of $\log_e OD_t$ and $1/OD_t$ are also linear, the slopes being $-k_1$ and $2k_2 / \epsilon l$ respectively.

When there exists a stoichiometric relationship between absorbing reactants (e. g. I_2^-) and absorbing product (I_3^-) allowance can be made for product absorption by use of a combined extinction coefficient.

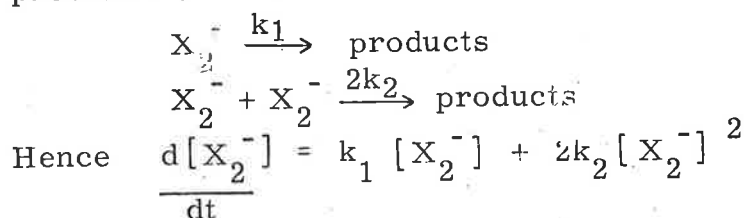
For example:



which exhibits linear plots of $1/OD_t$ against time, but calculation of the rate constant requires the use of an apparent extinction coefficient of $(\epsilon_{I_2^-} - \frac{1}{2}\epsilon_{I_3^-})$.

3.4.2 Competing first and second order reactions

In most instances the changes occurring cannot be analysed in terms of a simple first or second order reaction. In many cases halogen radical anions disappear by concurrent first and second order processes.



Integration of this rate law requires that

$$\log_e \left(\frac{[X_2^-]_t}{2k_2 [X_2^-]_t + k_1} \right) = -\log_e \left(\frac{[X_2^-]_0}{2k_2 [X_2^-]_0 + k_1} \right) - k_1 t$$

This expression requires knowledge of the rate constants $2k_2$ and k_1 and is of little use in situations where they are unknown. It is best used as a diagnostic test of mechanism when rate constants have been estimated by another method.

If, as is the case with halogen radical anions, the second order rate constant, $2k_2$, is known from independent experiments a simple numerical integration procedure using estimated values of

k_1 and the known value of $2k_2$ can be used to attempt to fit the experimental concentration against time curve with a theoretical one. Several values of k_1 can be tried and in interpolation method used to estimate the best fit value. Program FIT (Appendix 4.3) has been designed for this purpose.

3.4.3 Complex reaction schemes

Reaction schemes more complex than in 3.4.2 or situations in which more than one species is absorbing are best treated by a computer fit method. Program WR16 (Schmidt, 1966) has been adapted to suit this purpose (Appendix 4.4). It is capable of handling up to 30 reactions and 27 reactants. There are several approaches to kinetic problems in which this procedure is of great assistance, for example :-

(a) If a complex mechanism is proposed, the relative importance of individual steps is ascertained by fixing all rate constants but one, and observing the effect varying this rate constant on the concentration against time curve produced.

(b) If the mechanism is known but rate constants are not, they can be adjusted to fit the experimental concentration against time curve.

(c) If a mechanism is known but assumptions must be made to derive a simple kinetic relationship, the validity of these assumptions can be tested.

This list is not exhaustive. This technique of computer simulation is probably the most valuable technique in handling complex reaction schemes.

SECTION 4 - RADIATION CHEMISTRY

Section 4 discusses the reactions of halogen radical anions studied by pulse radiolysis. As a prerequisite to understanding these reactions knowledge of the reactions leading to production of the radical anions from hydroxyl radicals is necessary. In turn, an understanding of the primary processes involved in the formation of hydroxyl radicals is advantageous. In sections 4.1 and 4.2 a very brief and simplified resumé of the complicated history and currently accepted theories of primary radiation chemical processes is given. Section 4.3 discusses the reactions of aquated electrons with some commonly used scavengers. The significance of electron scavengers will become apparent when reactions of halogen radical anions produced by radiation chemical and photochemical techniques are discussed. (Sections 4.7 - 4.9, 5.3 - 5.5)

4.1 HISTORICAL

Shortly after the discovery of radioactivity, the first reports on the effect of this radiation on chemical systems were published, and in 1908 Cameron & Ramsay studied the effect of radon α -rays on water. For the next 50 years the complexity of the chemical processes occurring in water prevented a clear understanding of the primary radiation chemical processes. Reviews of the subject by Allen (1961) and Draganic & Draganic (1971) illustrate some of the problems encountered.

In the development of flash photolysis, Norrish & Porter (1949) used high energy single light flashes to study reactions in photochemical systems. The development of high energy electron sources which could readily be programmed to give single sub-microsecond pulses of radiation, whilst still delivering enough energy to produce detectable chemical changes from a single pulse, enabled pulse radiolysis to be

developed. Similar observation techniques to flash photolysis were employed. (For example see 2.1). The potentialities of the technique were quickly realized and it has now become an invaluable aid to radiation chemists. (Matheson & Dorfman, 1969).

4.2 PRIMARY PROCESSES IN THE RADIATION CHEMISTRY OF WATER

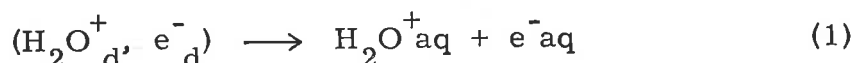
4.2.1 Energy deposition

Interaction of all forms of high energy radiation with water leads to ionization, in most cases producing secondary electrons of sufficient energy to cause ionization themselves. An understanding of the interactions of high energy electrons with water is fundamental to all radiation chemistry. As an electron or charged particle passes a water molecule, the electrons in the water molecule are excited. The slower or less energetic the particle, the longer it stays in the vicinity of a particular water molecule and hence the greater will be its effect on the bonding electrons. Some electrons are excited to a dissociation or ionization level producing what is now believed to be a pair of oppositely charged ions H_2O^+ and e^- within a solvent cage (Bevan & Hamill, 1970). Some of the excited electrons may themselves have sufficient energy to break clear of the parent molecule and cause further ionization of surrounding molecules. The energy of these so called secondary electrons is less than that of the primary electrons and consequently the ionizations produced are much closer together. The track produced by a single high speed electron in water can be visualized as a long straight track of infrequently spaced ionization with occasional clusters or "spurs" of ionized molecules caused by secondary electrons (Allen, 1961).

4.2.2 Solvation and spur reactions

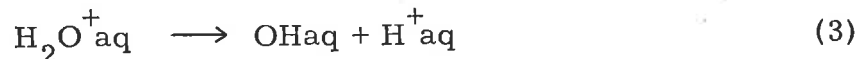
The ionized molecules within their solvent cage may either diffuse from or reorient the solvent cage around them to become

separate species or may become collisionally deactivated and recombine to form a water molecule.



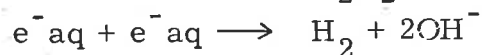
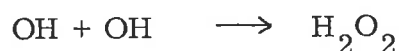
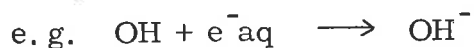
There is some evidence that if very high ($\sim 1 \text{ mol l}^{-1}$) concentrations of scavengers are present in solution the number of radicals reacting is greater than the number observed in the bulk of the solution. This suggests that reaction with the unsolvated ion pair may be taking place in competition with the geminate recombination (2). (Bevan & Hamill, 1970; Sawai & Hamill, 1970).

Formation of aquated electrons and hydroxyl radicals from ionized molecules is very rapid.



The fastest observations so far made have been about 20 ps after the absorption of energy and it appears that the species then observed are kinetically and observationally indistinguishable from the species observed after several microseconds (Bronskill, Wolff, & Hunt, 1969, 1970; Peled & Czapski, 1971; Hunt, Wolff, Bronskill, Jonah, Hart & Matheson, 1973).

Within the "spurs" radical concentrations are much higher than in the rest of the solution and before diffusion out of the "spur" can take place many radicals are lost by radical-radical reactions.



It is possible that the small yields of molecular products, H_2 and H_2O_2 , and hydrogen atoms are formed in spur reactions.

4.2.3 Bulk reactions

Fortunately the non-homogenous spur reactions are over in about 1 ns and the primary radiation products can then be treated as uniformly distributed over the bulk of the solution. The yields of

various species in the bulk of solution are expressed by G values (molecules produced per 100 eV absorbed). Values below are from Hart & Anbar (1970).

$$G(e^{-}aq) = 2.6$$

$$G(H^{+}) = 2.8$$

$$G(OH^{-}) = 0.1$$

$$G(OH) = 2.6$$

$$G(H) = 0.5$$

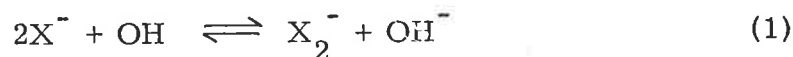
$$G(H_2) = 0.45$$

$$G(H_2O_2) = 0.7$$

In dilute aqueous solutions reactions of the solute occur only with radicals which have diffused into the bulk of the solution. In halide solutions, for example, electrons and hydrogen atoms may react with added electron scavengers (see 4.3) whilst hydroxyl radicals react with halide ions to produce halogen radical anions. (See 4.4, 4.5, 4.6)

4.3 ELECTRON SCAVENGERS

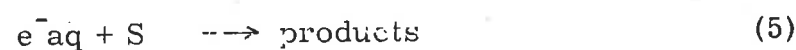
Radiation chemical formation of halogen radical anions requires only the presence of hydroxyl radicals. Aqueated electrons and hydrogen atoms only complicate the system by competing with halide ions for hydroxyl radicals,



or reacting with halogen radical anions (see 4.7)

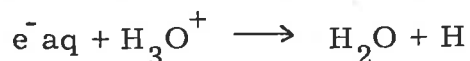


It is desirable to remove electrons by addition of various reactive substrates, collectively called electron scavengers.



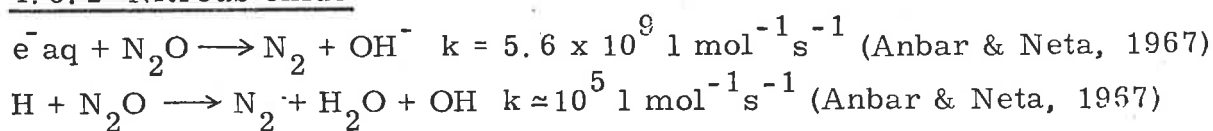
4.3.1 Acids

Aquated electrons react rapidly ($k \approx 2.3 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$; Anbar & Neta, 1967)[#] with hydronium ions to form hydrogen atoms



If hydrogen atoms do not interfere or are in turn scavenged, this maybe an effective method of eliminating complicating radicals from the system.

4.3.2 Nitrous oxide

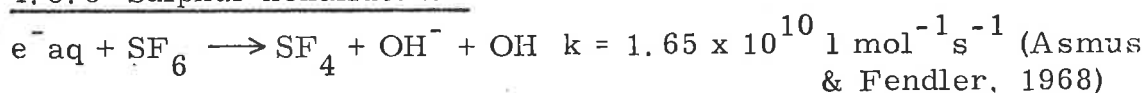


Nitrous oxide is soluble in water to the extent of about $10^{-2} \text{ mol l}^{-1}$ (Stephen & Stephen, 1963). At this concentration it will remove aquated electrons in less than 100 ns, resulting in the formation of an equal concentration of hydroxyl radicals, effectively eliminating the complications caused by electrons and simultaneously doubling the hydroxyl radical yield.

$$G(\text{OH})_{\text{N}_2\text{O}} = G(\text{OH}) + G(\text{e}^{-}\text{aq}) = 5.2$$

Hydrogen atoms react only slowly with nitrous oxide and are not efficiently scavenged.

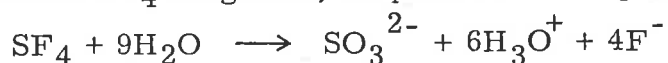
4.3.3 Sulphur hexafluoride



Footnote

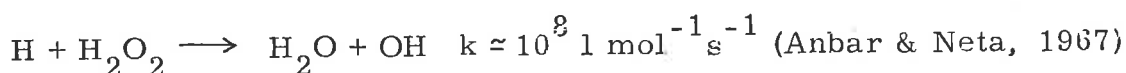
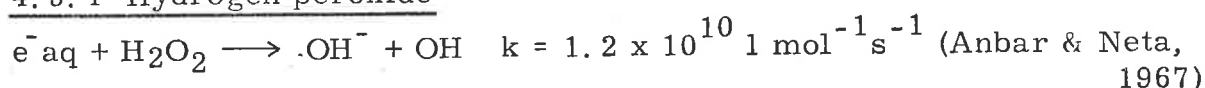
The rate constant quoted is an average of all values compiled by Anbar & Neta, (1967). Most of the fundamental e^{-}aq rate constants are well documented; original references are contained in the above compilation.

In some laboratories sulphur hexafluoride has replaced nitrous oxide as an electron scavenger. There is little to choose in reactivity or solubility and both form hydroxyl radicals. Sulphur hexafluoride itself is relatively inert to redox agents but the hydrolysis products of the reduced SF_4 fragment, in particular sulphite,

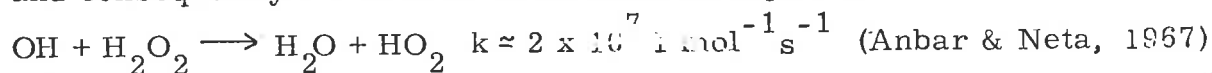


react with oxidising agents (OH or H_2O_2). Nitrous oxide does not suffer from this complication.

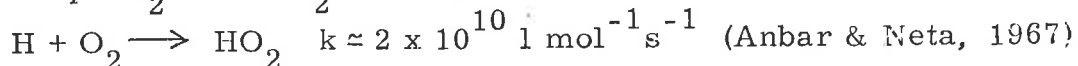
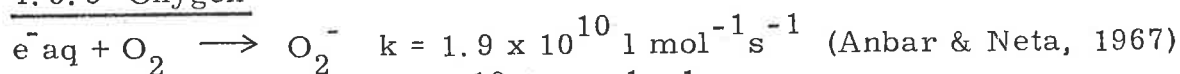
4.3.4 Hydrogen peroxide



Hydrogen peroxide reacts with aquated electrons and hydrogen atoms producing hydroxyl radicals. Its effectiveness in simplifying reaction schemes is limited because it also reacts with hydroxyl radicals and consequently its concentration must be kept within narrow limits



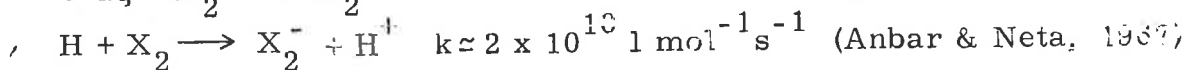
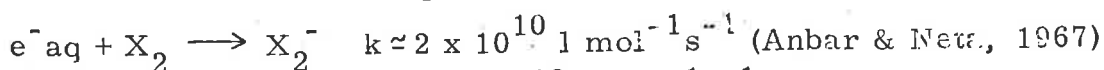
4.3.5 Oxygen



The effectiveness of oxygen as an electron scavenger or hydrogen atom scavenger is limited by its solubility ($\sim 10^{-3} \text{ mol l}^{-1}$; Stephen & Stephen, 1963) and the reactivity of radicals produced. The reaction scheme is seldom sufficiently simplified by the conversion of electrons to the mildly oxidising or reducing hydroperoxy radicals.

4.3.6 Halogens

For the study of halogen radical anion reactions halogens are effective electron scavengers.



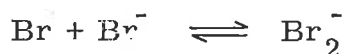
The reducing radicals are rapidly removed with a corresponding increase in the yield of halogen radical anions.

$$G(X_2^-)_{X_2} = G(OH) + G(e^-_{aq}) + G(H) = 5.7$$

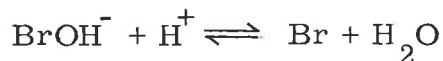
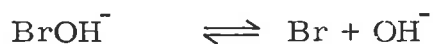
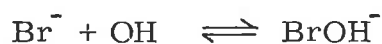
Provided that the presence of halogen does not interfere with other components of the system, for example reactive metal ions, they are very effective scavengers.

4.4 FORMATION OF Br_2^- FROM OH

Linnenbom & Cheek (1965) suggested that the formation of Br_2^- from hydroxyl radicals produced in the radiolysis of aqueous solutions was a simple two stage equilibrium.

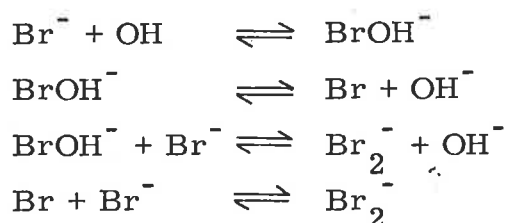


Matheson, Mulac, Weeks and Rabani (1966) found the rate of formation was pH dependent, an observation that cannot be satisfactorily explained by this simple mechanism. They suggested the formation of the intermediate $BrOH^-$, which can react with H_3O^+ or simply dissociate, to explain the pH dependence. This intermediate has since been detected in irradiated aqueous glasses containing Br^- (Marov & Symons, 1971) and a similar intermediate, $HOSCN^-$, has been observed in the oxidation of thiocyanate ions by hydroxyl radicals (Behar, Bevan & Scholes, 1971)

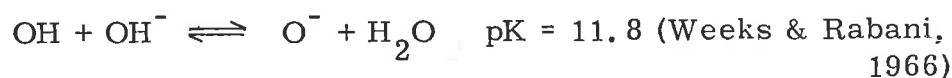


Recently simultaneous studies on the reactions have been published by Zehavi & Rabani (1972) and Behar (1972). Zehavi & Rabani report rate constants for the reactions in the scheme of Matheson et al (1966) in the acid or neutral region. Behar studied the equilibrium constants for formation of Br_2^- from OH in the pH

region 9 to 11.5. In this range the results were explained by the following scheme.



A combined reaction scheme to cover the pH range 0 to 11.5 can be written using the most reliable of the above values. Derived and selected equilibrium and kinetic properties are self consistent, and consistent with available experimental and thermodynamic data. Above pH 11.5 complications arise because hydroxyl radicals are deprotonated and may react at different rates.

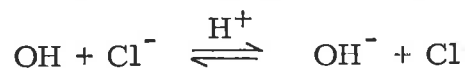


We have made no specific measurements on the formation of Br_2^- but the tabulated values (See Table 4.4A) are consistent with our experimental observations.

4.5 FORMATION OF Cl_2^- FROM OH

4.5.1 Literature data

The formation of Cl_2^- from hydroxyl radicals has not been as thoroughly investigated as that of Br_2^- . The only pulse radiolysis study is by Anbar and Thomas (1964). In acid solution (pH less than 3) the yield of Cl_2^- was independent of $[\text{Cl}^-]$ (above $10^{-3} \text{ mol l}^{-1}$) and corresponded to $G(\text{OH})$, but in neutral solution $G(\text{Cl}_2^-)$ depended on $[\text{Cl}^-]$ (up to 3 mol l^{-1}) and was less than that in acid solution. They interpreted these results as an acid dependent equilibrium, counteracted in neutral solution by spur effects.



The results agreed with the results of steady irradiation

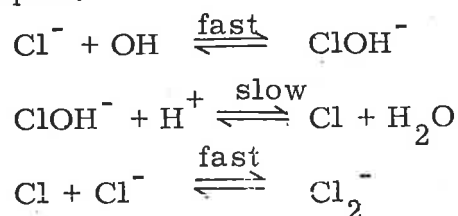
Table 4.4A

1) $\text{Br}^- + \text{OH}^- \rightleftharpoons \text{BrOH}^-$	$k_1 = (1.06 \pm 0.08) \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$	(a)
	$K_1 = 320 \pm 30 \text{ l mol}^{-1}$	(b)
	$k_{-1} = (3.3 \pm 0.4) \times 10^7 \text{ s}^{-1}$	(c)
2) $\text{BrOH}^- \rightleftharpoons \text{Br} + \text{OH}^-$	$k_2 = (4.2 \pm 0.6) \times 10^6 \text{ s}^{-1}$	(d)
	$K_2 = (2 \pm 0.5) \times 10^{-4} \text{ l mol}^{-1}$	(e)
	$k_{-2} = (2.2 \pm 0.5) \times 10^{10} \text{ l mol s}^{-1}$	(f)
3) $\text{BrOH}^- + \text{Br}^- \rightleftharpoons \text{Br}_2^- + \text{OH}^-$	$k_3 = (1.9 \pm 0.3) \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$	(g)
	$K_3 = 33 \pm 15$	(h)
	$k_{-3} = (6 \pm 3) \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$	(i)
4) $\text{BrOH}^- + \text{H}^+ \rightleftharpoons \text{Br} + \text{H}_2\text{O}$	$k_4 = (1.4 \pm 0.8) \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$	(j)
	$K_4 = (2.7 \pm 1) \times 10^8$	(k)
	$k_{-4} = (1.6 \pm 1) \times 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$	(l)
5) $\text{Br} + \text{Br}^- \rightleftharpoons \text{Br}_2^-$	$k_5 = 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$	(m)
	$K_5 = (2.2 \pm 1) \times 10^5 \text{ l mol}^{-1}$	(n)
	$k_5 = (4.5 \pm 2) \times 10^4 \text{ s}^{-1}$	(o)
6) $\text{OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}$	$K_6 = 1.8 \times 10^{12} \text{ l mol}^{-1}$	(p)

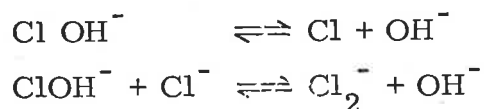
Footnotes and References - Table 4.4A

- (a) Zehavi & Rabani (1972)
- (b) Zehavi & Rabani (1972)
- (c) Zehavi & Rabani (1972)
- (d) Zehavi & Rabani (1972)
- (e) $K_2 = k_2/k_{-2}$
- (f) $k_{-2}/k_4 = 2.2$ (Matheson, Mulac, Weeks & Rabani; 1966)
- (g) Zehavi & Rabani (1972)
- (h) $K_1 K_3 = (1.06 \pm 0.3) \times 10^4 \text{ l mol}^{-1}$ (Behar, 1972)
- (i) $k_{-3} = k_3/K_3$
- (j) Zehavi & Rabani (1972)
- (k) $2\text{Br}^- + \text{OH} + \text{H}^+ \rightleftharpoons \text{Br}_2^- + \text{H}_2\text{O}$
 $K \text{ over all} = K_1 K_2 K_5 K_6 = K_1 K_3 K_6 = K_1 K_4 K_5$
hence $K_4 = K_3 K_6 / K_5$
- (l) $k_{-4} = k_4/K_4$
- (m) Cercek, Ebert, Gilbert and Swallow (1965), Matheson et al. (1966)
- (n) Cercek et al. (1965)
- (o) Cercek et al. (1965)
- (p) $K_6 = K_w^{-1}$; $K_w = 10^{-14} \text{ mol l}^{-1}$

competition studies which had indicated a pH dependence of the (Cl^- , OH) rate constant (Allen, 1961). To explain these results and the observation that the rate constant showed the ionic strength dependence expected for a 1 +, 1 - reaction, Anbar and Thomas (1964) proposed the formation of HOCl^- the existence of which in the solid state has since been confirmed (Ginns & Symons, 1972), in a fast pre-equilibrium, followed by the rate determining reaction of H^+ with this complex



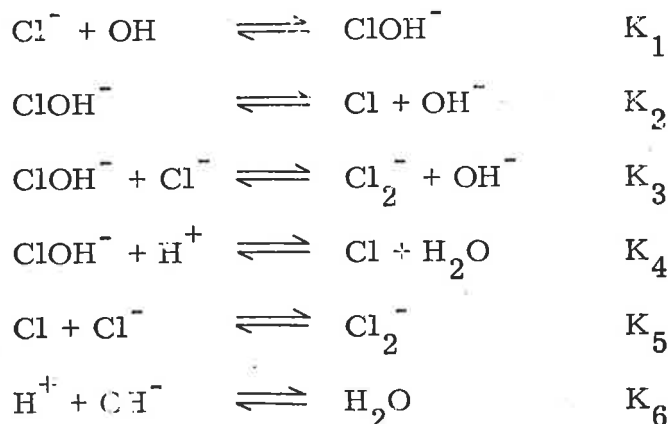
The alternative equilibria



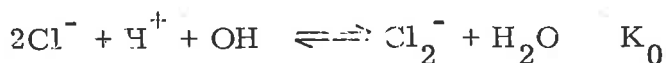
which were important in the analogous Br^- reaction (See 4.4) should also be considered as possible paths.

4.5.2 Equilibrium expressions

The formation of Cl_2^- from OH can be represented by:



The overall equilibrium constant,



must, from the stoichiometry, be related by

$$\begin{aligned}
 K_0 &= K_1 K_2 K_5 K_6 \\
 &= K_1 K_3 K_6 \\
 &= K_1 K_4 K_5
 \end{aligned}$$

If the assumption that Cl_2^- is the only absorbing species at 365 nm is made then expressions for the maximum absorbance as a function of pH and Cl^- concentration can be derived.

(a) At high $[\text{Cl}^-]$ ($\geq 2 \times 10^{-3} \text{ mol l}^{-1}$) ClOH^- & Cl_2^- are the only species in significant concentration at equilibrium

$$G(\text{OH}) = G(\text{Cl}_2^-)_\infty = G(\text{Cl}_2^-) + G(\text{ClOH}^-)$$

where $G(\text{Cl}_2^-)_\infty$ is the Cl_2^- yield under conditions where Cl_2^- is the only significant radical species.

Comparing the absorbance due to Cl_2^- when equilibrium is attained D , with that when $G(\text{OH}) = G(\text{Cl}_2^-)$, D_∞

$$\frac{D_\infty}{D} = \frac{[\text{ClOH}^-] + [\text{Cl}_2^-]}{[\text{Cl}_2^-]} \quad \dots \textcircled{1}$$

From equilibrium (3)

$$K_3 = \frac{[\text{Cl}_2^-] \cdot [\text{OH}^-]}{[\text{ClOH}^-][\text{Cl}^-]}$$

$$\therefore \frac{[\text{ClOH}^-]}{[\text{Cl}_2^-]} = \frac{[\text{OH}^-]}{K_3 [\text{Cl}^-]}$$

$$\therefore \frac{D_\infty}{D} = \frac{[\text{OH}^-]}{K_3 [\text{Cl}^-]} + 1 \quad \dots \textcircled{2}$$

(b) At low $[\text{Cl}^-]$

At equilibrium, OH , ClOH^- , Cl , and Cl_2^- coexist and expression $\textcircled{1}$ becomes.

$$\frac{D_\infty}{D} = \frac{[\text{OH}] + [\text{ClOH}^-] + [\text{Cl}] + [\text{Cl}_2^-]}{[\text{Cl}_2^-]} \quad \dots \textcircled{3}$$

From equilibrium (5)

$$K_5 = \frac{[Cl_2^-]}{[Cl][Cl^-]}$$

$$\frac{[Cl]}{[Cl_2^-]} = \frac{1}{K_5 [Cl^-]}$$

From equilibrium (1)

$$K_1 = \frac{[ClOH^-]}{[Cl^-][OH]}$$

$$\frac{[OH]}{[ClOH^-]} = \frac{1}{K_1 [Cl^-]}$$

From equilibrium (3)

$$\frac{[ClOH^-]}{[Cl_2^-]} = \frac{[OH^-]}{K_3 [Cl^-]}$$

$$\frac{[OH]}{[Cl_2^-]} = \frac{[OH^-]}{K_1 K_3 [Cl^-]^2}$$

Substituting in (3) one obtains

$$\frac{D_\infty}{D} = \frac{[OH^-]}{K_1 K_3 [Cl^-]^2} + \frac{[OH^-]}{K_3 [Cl^-]} + \frac{1}{K_5 [Cl^-]} + 1 \quad \dots (4)$$

$$\frac{D_\infty}{D} = [OH^-] \left(\frac{1 + K_1 [Cl^-]}{K_1 K_3 [Cl^-]^2} \right) + \left(\frac{1}{K_5 [Cl^-]} + 1 \right) \quad \dots (5)$$

4.5.3 Evaluation of equilibrium constants

From expression (5), at a fixed $[Cl^-]$ a plot of D_∞/D against $[OH^-]$ should be a straight line of slope

$$S_5 = \frac{1 + K_1 [Cl^-]}{K_1 K_3 [Cl^-]^2} \quad \dots (6)$$

and intercept

$$I_5 = \frac{1}{K_5 [Cl^-]} + 1 \quad \dots (7)$$

At various Cl^- concentrations a plot of I_5 against $1/[\text{Cl}^-]$ should be a straight line of slope. ^{55.}

$$S_7 = \frac{1}{K_5}$$

Figure 4.5A shows plots of D_∞/D against $[\text{OH}^-]$ at four Cl^- concentrations. Figure 4.5B shows a plot of I_5 against $1/[\text{Cl}^-]$ from which at $22 \pm 2^\circ\text{C}$ and ionic strength = 0.70 mol l^{-1} .

$$K_5 = 6 \times 10^4 \text{ l mol}^{-1}$$

From expression (6) one obtains

$$S_5 \cdot [\text{Cl}^-] = \frac{1}{K_1 K_3 [\text{Cl}^-]} + \frac{1}{K_3} \quad \dots \quad (8)$$

Figure 4.5C shows a plot of $S_5 \cdot [\text{Cl}^-]$ against $1/[\text{Cl}^-]$ from which

$$S_8 = \frac{1}{K_1 K_3} = 10^4 \text{ mol l}^{-1}$$

$$\text{and } I_8 = \frac{1}{K_3} = 2.2 \times 10^9$$

$$\therefore K_3 = 4.5 \times 10^{-10}$$

$$\text{and } K_1 = 2 \times 10^5 \text{ l mol}^{-1}$$

$$\begin{aligned} \text{Now } K_0 &= K_1 K_2 K_5 K_6 \\ &= K_1 K_3 K_6 \\ &= K_1 K_4 K_5 \\ &= 1.8 \times 10^8 \text{ l}^2 \text{ mol}^{-2} \end{aligned}$$

$$\therefore K_4 = 1.6 \times 10^{-2}$$

$$\text{and } K_2 = 9 \times 10^{-15} \text{ mol l}^{-1}$$

These equilibrium constants can be checked by comparing the observed and expected results under conditions of high $[\text{Cl}^-]$ ($> 2 \times 10^{-3} \text{ mol l}^{-1}$). From expression (2) in 4.5.2

$$\frac{D_\infty}{D} = \frac{[\text{OH}^-]}{K_3 [\text{Cl}^-]} + 1$$

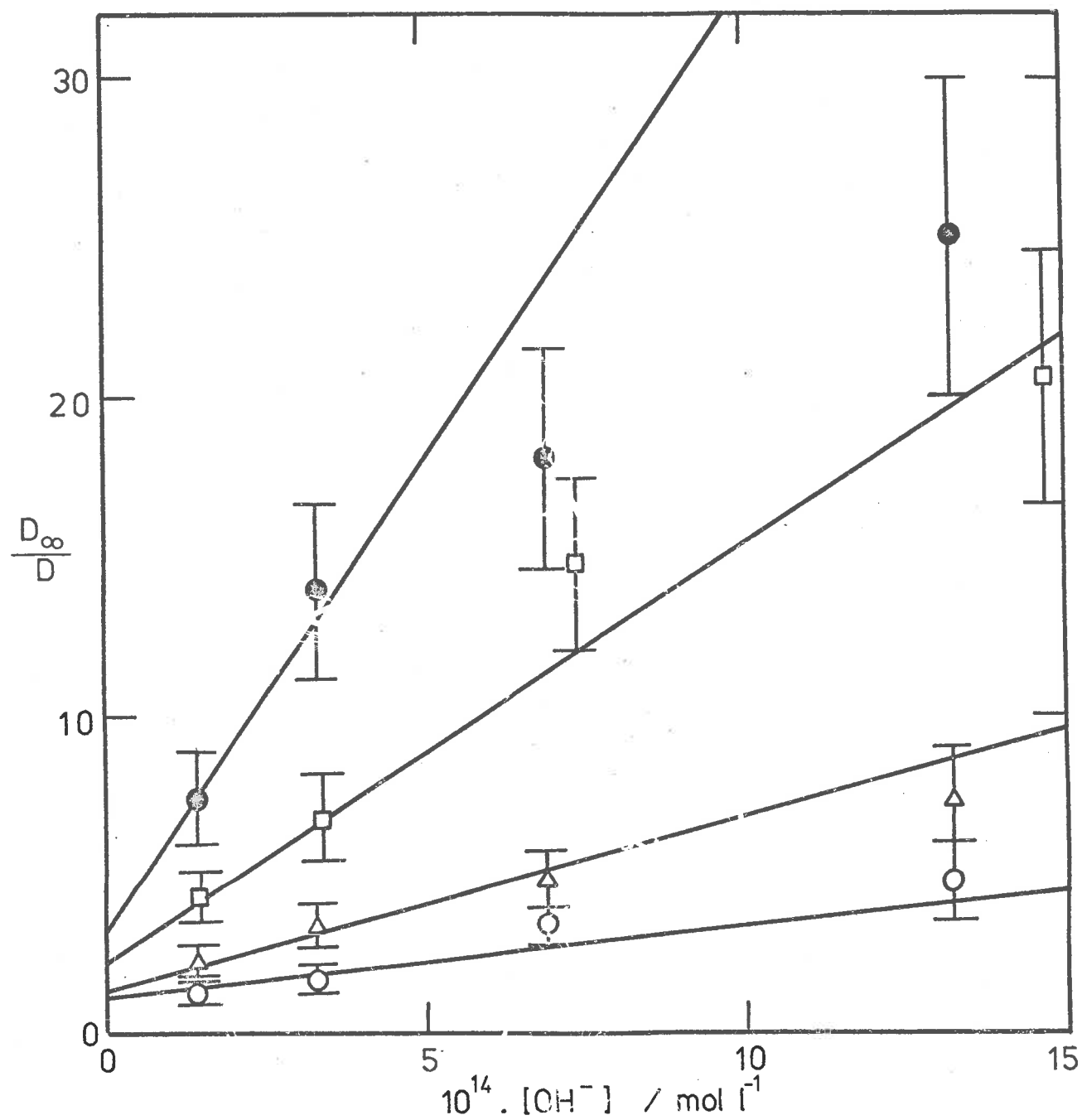
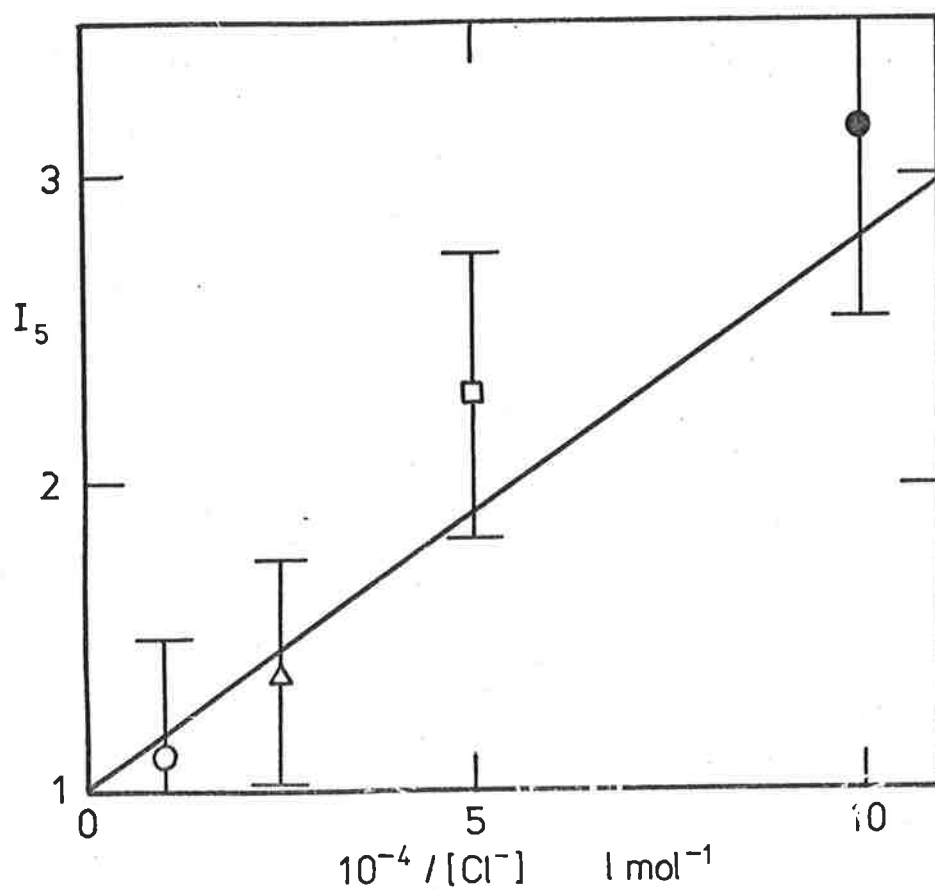


Fig. 4.5A Cl_2^- Formation (Cl^- ; $\bullet, 10^{-5}$; $\square, 2 \times 10^{-5}$; $\triangle, 4 \times 10^{-5}$; $\circ, 10^{-4}$ mol l $^{-1}$)



Figs. 4.5B, 4.5C Cl_2^- Formation

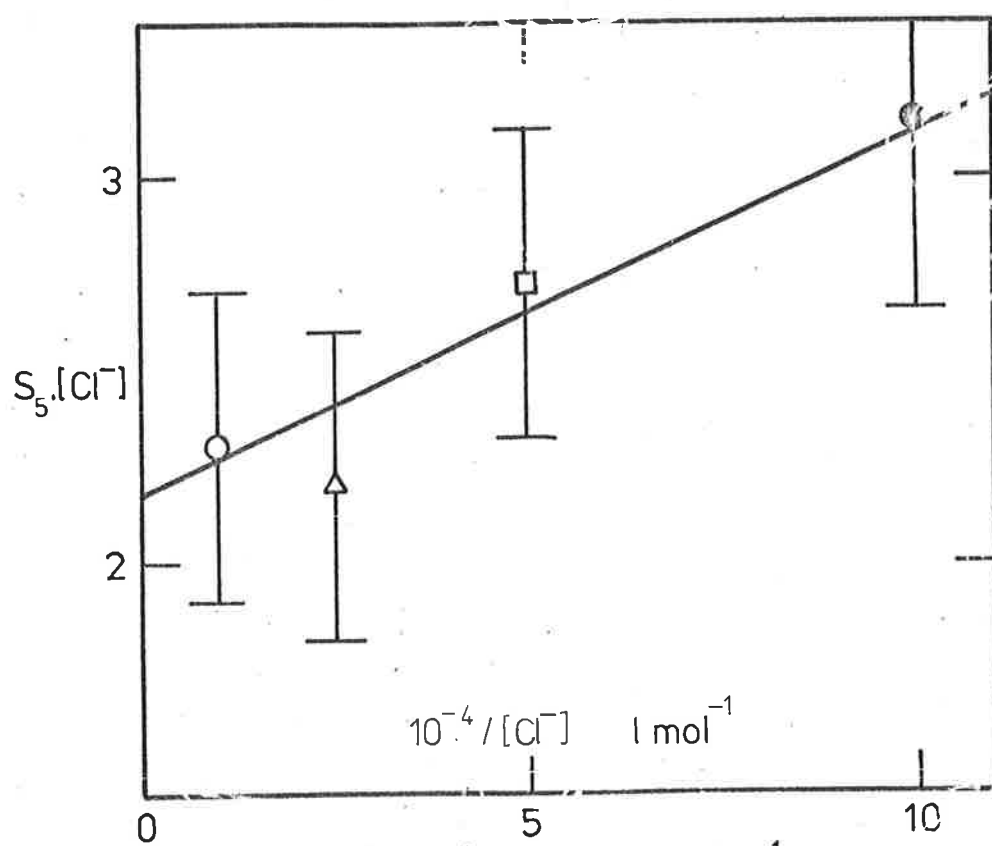


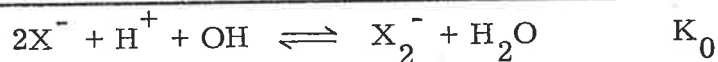
Figure 4.5D shows a plot of experimental D_{∞}/D values against $[\text{OH}^-]/[\text{Cl}^-]$. The straight line is calculated using the previously determined value of K_3 . The agreement is satisfactory. Table 4.5A lists the derived equilibrium constants.

4.5.4 Comparison with literature values

Anbar and Thomas (1964) made only a few observations on the Cl_2^- yield as a function of pH and $[\text{Cl}^-]$. Their results in the acid pH region are in qualitative agreement with ours, in that the Cl_2^- yield starts to drop when $[\text{OH}^-]/[\text{Cl}^-]$ is greater than about 10^{-10} .

At neutral pH they observed Cl_2^- if $[\text{Cl}^-]$ was greater than 0.3 mol l^{-1} , an effect they attributed to spur reactions. From the current results the equilibrium ratio of the Cl_2^- to OH can be calculated as a function of $[\text{Cl}^-]$. Even at 1 mol l^{-1} concentrations of Cl^- , expression 2 (4.5.2) predicts that the less the 0.5% of OH are converted to Cl_2^- at equilibrium. The conclusion of Anbar and Thomas that at pH 7, Cl_2^- is formed only in the spurs, which are regions of high acidity, appears to be correct.

4.5.5 Comparison with thermodynamic quantities



From data in Table 4.5A and 4.4A one can obtain:-

$$K_0(\text{Cl}^-) = 1.8 \times 10^8 \text{ l}^2 \text{ mol}^{-2}$$

$$\text{and } K_0(\text{Br}^-) = 1.9 \times 10^{16} \text{ l}^2 \text{ mol}^{-2}$$

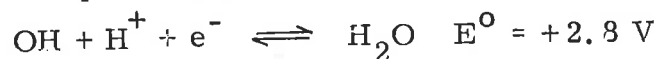
from the expression

$$\Delta G^0 = -nFE^0 = -RT \ln K$$

one can calculate $\Delta E^0(\text{Cl}^-) = 0.50 \text{ V}$

$$\Delta E^0(\text{Br}^-) = 0.98 \text{ V}$$

The OH, OH^- couple in acid solution is assumed to be



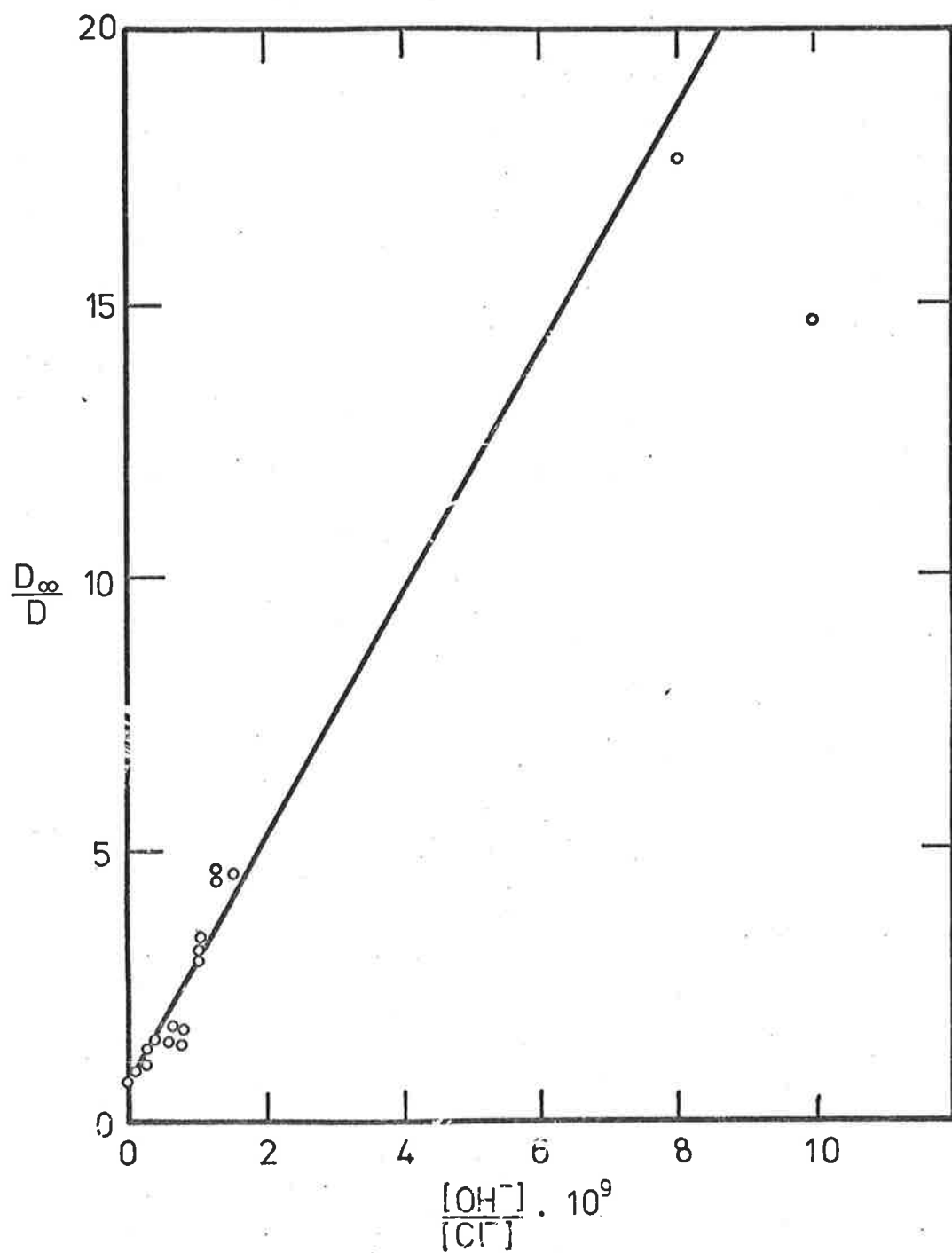


Fig. 4.5D Cl_2^- Formation

Table 4.5A

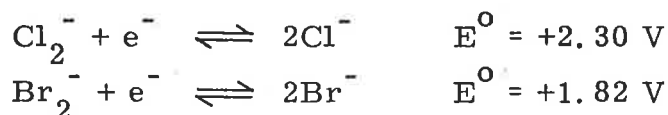
1)	$\text{Cl}^- + \text{OH}^- \rightleftharpoons \text{ClOH}^-$	$K_1 = (2 \pm 1) \times 10^5 \text{ l mol}^{-1}$	(a)
2)	$\text{ClOH}^- \rightleftharpoons \text{Cl} + \text{OH}^-$	$K_2 = (9 \pm 4) \times 10^{-15} \text{ mol l}^{-1}$	(a)
3)	$\text{ClOH}^- + \text{Cl}^- \rightleftharpoons \text{Cl}_2^- + \text{OH}^-$	$K_3 = (5 \pm 2) \times 10^{-10}$	(a)
4)	$\text{ClOH}^- + \text{H}^+ \rightleftharpoons \text{Cl} + \text{H}_2\text{O}$	$K_4 = (1.6 \pm 0.8) \times 10^{-2}$	(a)
5)	$\text{Cl} + \text{Cl}^- \rightleftharpoons \text{Cl}_2^-$	$K_5 = (6 \pm 2) \times 10^4 \text{ l mol}^{-1}$	(a)
6)	$\text{OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}$	$K_6 = 1.8 \times 10^{12} \text{ l mol}^{-1}$	(b)

Footnotes and References Table 4.5A

(a) This work

(b) $K_6 = 1/K_w \text{ H}_2\text{O}$; $K_w = 10^{-14} \text{ mol l}^{-1}$

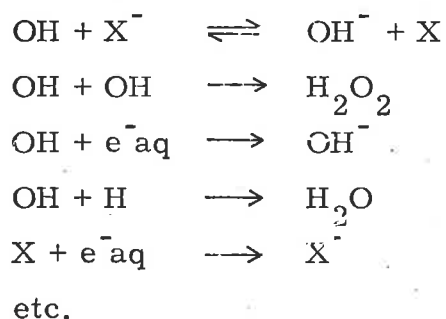
from which it can be calculated



values which compare favourably with the values of +2.29 and +1.77 V calculated from thermodynamic quantities (Appendix 2.3).

4.5.6 Rate of formation of Cl_2^-

The rate of formation of Cl_2^- depends both on $[\text{Cl}^-]$ and $[\text{H}^+]$ in the pH region of 0 - 4. Anbar and Thomas made observations on this rate but did not evaluate individual rate constants. The use of 2 μs pulse of radiation makes rate measurements on the formation of Cl_2^- very difficult, because sufficiently low chloride and acid concentrations to observe a subsequent formation, must be used, with the result that other radical reactions become important.



The use of a nanosecond pulse facility would greatly simplify the rate measurements.

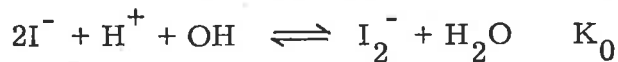
The observed rates of formation of Cl_2^- are in qualitative agreement with those observed by Anbar and Thomas (1964). We have made no estimates of rate constants involved.

4.6 FORMATION OF I_2^- FROM OH

4.6.1 Equilibrium constants

Baxendale and Bevan (1968, 1969) studied the yield of I_2^- in pulse radiolysed iodide solution as a function of I^- concentration and temperature. They did not investigate the effect of pH, but the observation of I_2^- at pH 7 is well established. (Baxendale and Bevan, 1969)

The overall equilibrium constant



can be calculated from thermodynamic data (cf 4.5.5) as $1 \times 10^{30} \text{ l}^2 \text{ mol}^{-2}$. Assuming that the equilibrium constant K_1



is, by analogy with ClOH^- and BrOH^- about 10 l mol^{-1} then the equilibrium constants in table 4.6A can be estimated (cf 4.4, 4.5)

Table 4.6A

$\text{I}^- + \text{OH}^- \rightleftharpoons \text{IOH}^-$	$K_1 = 10 \text{ l mol}^{-1}$
$\text{IOH}^- \rightleftharpoons \text{I} + \text{OH}^-$	$K_2 = 10^{12} \text{ mol l}^{-1}$
$\text{IOH}^- + \text{I}^- \rightleftharpoons \text{I}_2^-$	$K_3 = 10^{17}$
$\text{IOH}^- + \text{H}^+ \rightleftharpoons \text{I} + \text{H}_2\text{O}$	$K_4 = 10^{24}$
$\text{I} + \text{I}^- \rightleftharpoons \text{I}_2^-$	$K_5 = 1 \times 10^5 \text{ l mol}^{-1}$
$\text{OH}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}$	$K_6 = 1.8 \times 10^{12} \text{ l mol}^{-1}$

The large values of K_2 , K_3 and K_4 are large compared to the Cl^- or Br^- systems. It can be estimated that at pH 14 the equilibrium between OH and I is 99% in favour of I even at $[\text{I}^-] = 10^{-10} \text{ mol l}^{-1}$. The only effect of iodide concentration on the observation of I_2^- arises through its effect on equilibrium (5).

4.6.2 Rate constants

The rate of reaction of hydroxyl radicals with iodide is pH independent over the measured range (Anbar and Neta, 1967). The first pulse radiolysis study by Thomas (1965) gave a rate constant of $(1.2 \pm 0.13) \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ but did not distinguish the rate determining step.



Buxendale and Bevan (1969) reinvestigated the reaction with a

view to its suitability as a reference for competition kinetics but found that step (2) is rate limiting. They estimate

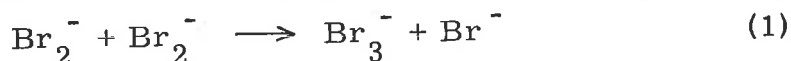
$$k_1 \sim 3 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$$

$$k_2 = 7.6 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$$

Under similar conditions to those used by Thomas (1965) the results are in quantitative agreement. We have made no measurements on the rate of formation of I_2^- .

4.7 DECAY OF Br_2^-

The major process removing Br_2^- in the absence of added reactive substrates is the disproportionation reaction (1).



Early pulse radiolysis studies of bromide by Sutton, Adams, Boag, and Michael (1965), Cercek, Ebert, Gilbert and Swallow (1965) and Matheson, Mulac, Weeks and Rabani (1966) observed the disproportionation. Using various electron scavengers they measured rate constants, $2k_1$, as shown in Table 4.7A. The average value of $3.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ has since been substantiated by flash photolysis studies (see 5.3).

4.7.1 Deaerated neutral bromide

In the absence of added electron scavengers Br_2^- decayed by a reasonable second order process after the first $1\frac{1}{2}$ half lives. In this initial period significant departure of the second order plots from linearity was observed. Matheson, Mulac, Weeks and Rabani (1966) also observed initial curvature which they attributed to reaction of aquated electrons with Br_2^- ($k_2 \approx 1.3 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$)

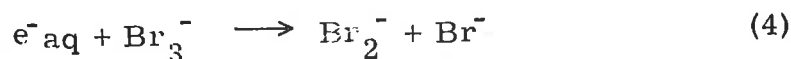
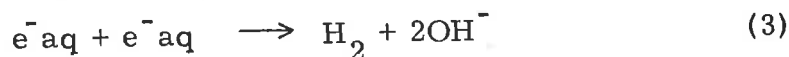
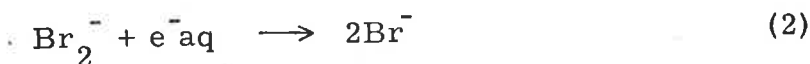
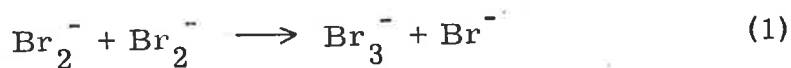


Table 4.7A

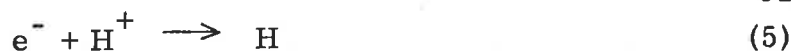
System	$2k_1 \times 10^{-9}$ ($\text{l mol}^{-1} \text{s}^{-1}$)	pH	$[\text{Br}^-]$ (mol l^{-1})	Ref
Br^- , Br_2	3.6 ± 0.7	2, 7	10^{-2}	a
Br^- , Br_2	4.2 ± 0.8	2	10^{-1}	a
Br^- , N_2O	3.6 ± 0.6	2, 7	10^{-2}	b
Br^-	3.3 ± 1	7	10^{-4} - 10^{-2}	c
Br^- , N_2O	4.5 ± 1	1	10^{-4}	c
Br^- , N_2O	3.3 ± 1	4-10	10^{-3}	c

References:

(a) Sutton, Adams, Boag and Michael (1965)

(b) Cercek, Ebert, Gilbert and Swallow (1965)

(c) Matheson, Mulac, Weeks and Rabani (1966)



etc.

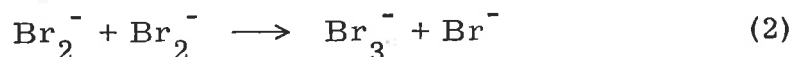
From the initial slope of the second order plot it can be estimated that $k_2 = (8 \pm 4) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, in reasonable agreement with the value of Matheson et al (1966). No attempt to computer fit pulse radiolysis decay curves in terms of the above scheme was made but in the analogous flash photolysis experiments good fits were obtained (see 5.3.1).

4.7.2 Acidified deaerated bromide

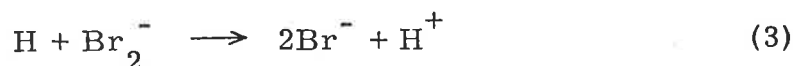
Aquated electrons are rapidly converted to hydrogen atoms by acid (see 4.3.1)



The second order decay curves for Br_2^- in acid solution are good second order after a slight initial curvature extending over about one half life. The second order decay has a rate constant of $3.7 \pm 0.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in good agreement with the rate of the disproportionation reaction (2)

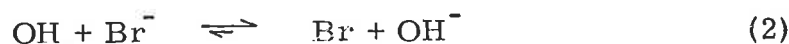
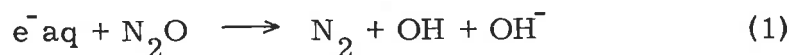


From the initial curvature which is attributed to reaction of hydrogen atoms with Br_2^- the rate constant k_3 can be estimated as $5 \pm 2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.



4.7.3 Nitrous oxide saturated bromide

Aquated electrons are rapidly converted to hydroxyl radicals by nitrous oxide (see 4.3.2). In the presence of excess bromide hydroxyl radicals produce more Br_2^- (see 4.4)





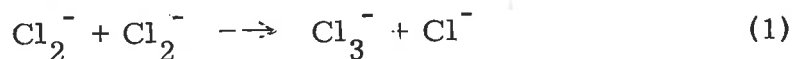
The decay of Br_2^- is very good second order with a rate constant $2k_4$ of $(3.3 \pm 0.6) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in excellent agreement with the value of $(3.6 \pm 0.6) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ obtained by Cercek, Ebert, Gilbert and Swallow (1965) in the same system.

4.7.4 Summary

The pulse radiolysis derived rate constants are compared with those from flash photolysis and literature values in section 5.3.11.

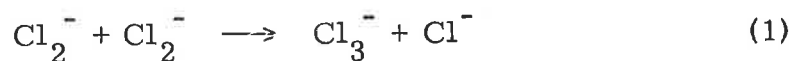
4.8 DECAy OF Cl_2^-

The reactions of Cl_2^- in pulse radiolysed chloride solution have not previously been studied. Flash photolysis studies have attributed the decay of Cl_2^- to the disproportionation reaction (1) but have failed to agree on a value for $2k_1$ (see 5.4).

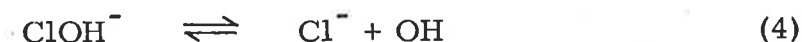
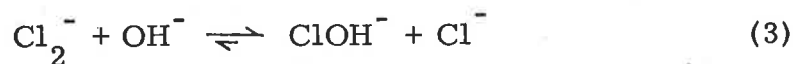


4.8.1 Deaerated neutral chloride

To produce measurable yields of Cl_2^- in neutral solution the concentration of $[\text{Cl}^-]$ must be above 0.3 mol l^{-1} (Anbar and Thomas 1964). In $0.5 \text{ mol l}^{-1} [\text{Cl}^-]$, second order plots for the decay of Cl_2^- show considerable curvature, analogous to, but more pronounced than, the curvature experienced in the corresponding bromide system. Compared to the bromide case the decay of Cl_2^- is further complicated by reactions reducing Cl_2^- to its initial bulk concentration (at $0.5 \text{ mol l}^{-1} [\text{Cl}^-]$, Cl_2^- is produced in the spur regions in excess of bulk equilibrium concentrations).



etc.

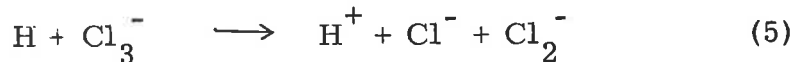
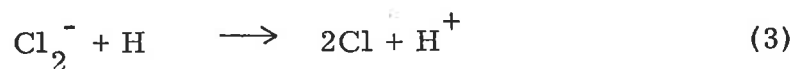
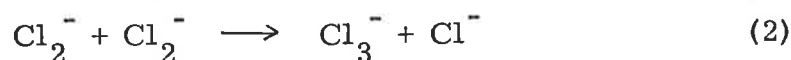


etc.

The reaction scheme is too complex to analyse by conventional means and contains too many unknown rate constants to use computer simulation. Comparison of the the initial and final slopes of the second order plot suggests $k_2 \approx (1 \pm 0.5) \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$.

4.8.2 Acidified deaerated chloride solution

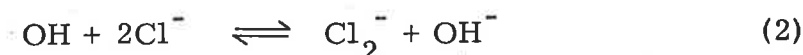
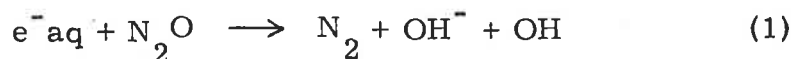
Addition of moderate ($\sim 10^{-2} \text{ mol l}^{-1}$) concentrations of acid allows one to drop the chloride concentration to about $10^{-2} \text{ mol l}^{-1}$ where Cl_2^- is formed in the bulk of solution rather than in the spur regions. The complicating re-equilibration reactions are consequently eliminated. Under these conditions the second order decay of Cl_2^- showed initial curvature over about two half lives, attributable to reaction of Cl_2^- with hydrogen atoms.



From initial and final slopes it can be estimated that $k_3 \approx (1 \pm 0.5) \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_2 \approx (5 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

4.8.3 Nitrous oxide saturated chloride solution

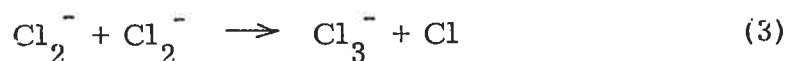
If nitrous oxide is to be an effective electron scavenger the pH must be above 4 (see 4.3.2). At this pH, high concentrations of chloride are required to convert hydroxyl radicals to Cl_2^- .



If reaction (2) is complete

$$G(Cl_2^-) = G(OH) + G(e^-_{aq}) \\ \approx 2G(OH)$$

Compared to the same solution without nitrous oxide where $G(Cl_2^-) = G(OH)$, a doubling of the yield of Cl_2^- should be observed. Within the limits of experimental error, this is achieved at pH 4 with $[Cl^-] = 0.5 \text{ mol l}^{-1}$. In this system the decay of Cl_2^- is excellent second order over at least 2 half lives with a rate constant $2k_3$ of $(6 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.



4.8.4 Summary

The rate constants derived in section 4.8 are compared with those from flash photolysis and literature values in 5.4.11.

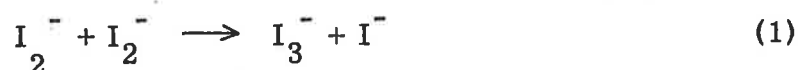
4.9 DECAY OF I_2^-

The rate of decay of I_2^- produced by pulse radiolysis of iodide solutions has not been measured. The disproportionation reaction (1) with a rate constant, $2k_1$, of $7.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ is well established as the major process by which I_2^- decays in flash photolysed iodide and iodine solutions (see 5.5)



4.9.1 Nitrous oxide saturated iodide solution

As expected, nitrous oxide approximately doubles the yield of I_2^- from an irradiated iodide solution (see 4.3.2). Observation at 335 nm where $\epsilon_{I_2^-} \approx \frac{1}{2}\epsilon_{I_3^-}$ confirms a 2:1 stoichiometry between I_2^- removed by disproportionation and I_3^- formed.



The decay of I_2^- (observed at 405 nm where $\epsilon_{I_2^-} > \frac{1}{2} \epsilon_{I_3^-}$) and the formation of I_3^- (observed at 313 nm where $\epsilon_{I_2^-} < \frac{1}{2} \epsilon_{I_3^-}$) are both good, second order with rate constants of $(8.0 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ and $(7.5 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ respectively. These values are in excellent agreement with those determined by flash photolysis methods (see 5.5)

SECTION 5 - FLASH PHOTOLYSIS

The majority of results in this thesis were obtained by flash photolysis techniques. As in Section 4 some knowledge of the distribution of radicals and the photochemical methods of production of halogen radical anions is a necessary pre-requisite to discussion of the decay processes involved. Photochemical methods of production of halogen radical anions have been discussed in 1.4

5.1 ABSORPTION OF PHOTOLYSING LIGHT - RADICAL YIELDS

5.1.1 Energy Dissipation

The output from the flash lamp is virtually a continuum (see 2.2.1). The light absorbed by the solution at a particular wavelength is expressed by the relation

$$\log_{10} \frac{I_o}{I_t} = OD = \sum_{i=1}^n \epsilon_i [C_i] \cdot l$$

where I_o is the incident light intensity
 I_t is the transmitted light intensity
 ϵ_i is the extinction coefficient of species i
 $[C_i]$ is the molar concentration of species i
 l is the depth of solution through which the light passes

In general only one species is responsible for the desired photochemical change and only light of suitable wavelengths for excitation of this species need be considered.

5.1.2 Overall yields

The concentration of radicals produced in a system depends upon the amount of effective light absorbed by the solution and the quantum efficiency of the photochemical process. The higher the optical density of the solution the more light is absorbed, consequently, unless secondary effects or back reactions are affected, the higher the active

solute concentration the greater the overall yield.

5.1.3 Effective yields

The physical arrangement for flash photolysis in this laboratory is such that observations are made on a section of solution in the centre of the cell about 1 cm for the side wall. To improve detection accuracy the concentration of radicals produced in this section should be maximized and in most cases balance between the following effects must be obtained.

- (a) Too small a solute concentration does not absorb enough light.
- (b) Too large a solute concentration absorbs almost all the light in the first 1 cm and the intensity of light reaching the effective region will be low.

The optimum concentration of solute depends upon the system being studied, for example, the optimum Br_3^- concentration is below $10^{-3} \text{ mol l}^{-1}$, the optimum Br^- concentration is between 10^{-2} and $10^{-1} \text{ mol l}^{-1}$ (see Table 5.3B), and the optimum chloride concentration is above 0.5 mol l^{-1} (see Table 5.4B).

5.1.4 Scavenger effects

Some of the photochemical systems used to produce halogen radical anions also produce other radicals, the most common being aquated electrons. Use of various electron scavengers (see 4.3) may aid in simplifying the resulting reaction schemes. It should be pointed out that some of the scavengers discussed (particularly H_2O_2 and halogens) are themselves photoactive and their photodecomposition products must be considered.

5.2 FORMATION OF HALOGEN RADICAL ANIONS

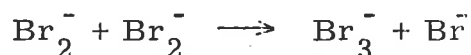
Photochemical formation of halogen radical anions proceeds through halogen atoms, hydroxyl radicals and aquated electrons (see 1.4). The formation of hydroxyl radicals from aquated electrons

(see 4.3.2, 4.3.3) and halogen radical anions from hydroxyl radicals (see 4.4, 4.5, 4.6) has been discussed in detail. Except for the primary processes involved, formation of halogen radical anions from pulse radiolysis and flash photolysis follows the same mechanism.

Because of the limited resolution time for flash photolysis measurements ($t > 30 \mu\text{s}$; see 2.4.6) it was impossible to make observations on the rate of formation of halogen radical anions in flash photolysis systems.

5.3 DECAY OF Br_2^-

In the absence of other reactive substances Br_2^- decays by the disproportionation reaction.

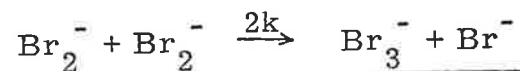


This is the best documented reaction of halogen radical anions, being agreed upon by five different groups.

Langmuir and Hayon (1967) studied the flash photolysis of bromide ion and mercuric bromide complexes and found that the decay of Br_2^- could be attributed to a second order reaction with a rate constant in good agreement with that obtained by pulse radiolysis. In the course of our investigation, Malone & Endicott (1972) reported values of the second order rate constant for decay of Br_2^- from nitrous oxide saturated bromide solution and solutions of halogenopentaamminecobalt (III) complexes. Pulse radiolysis determinations of the disproportionation rate constant have been discussed in section 4.7.

A summary of our measurements and the published values purporting to be for the disproportionation reaction are listed in Table 5.3A.

Table 5.3A



Year	Method*	System	$2k \times 10^{-9}$	pH	$[\text{Br}^-]$ (mol l ⁻¹)	Ref [†]
1965	pr	Br^-, Br_2	3.6 ± 0.7	2, 7	10^{-2}	a
1965	pr	Br^-, Br_2	4.2 ± 0.8	2	10^{-1}	a
1965	pr	$\text{Br}^-, \text{N}_2\text{O}$	3.6 ± 0.6	2, 7	10^{-2}	b
1966	pr	Br^-	3.3 ± 1	7	$10^{-4} - 10^{-2}$	c
1966	pr	$\text{Br}^-, \text{N}_2\text{O}$	4.5 ± 1	1	10^{-4}	c
1966	pr	$\text{Br}^-, \text{N}_2\text{O}$	3.3 ± 1	4-10	10^{-3}	c
1967	fp	Br^-	3.7 ± 0.6	6	2×10^{-2}	d
1967	fp	HgBr_2^{2-}	3.2 ± 0.1	6	2×10^{-2}	d
1972	fp	$\text{Br}^-, \text{N}_2\text{O}$	5.8 ± 1	1	1.0	e
1972	fp	$\text{CoA}_5\text{Br}^{2+}$	3.2 ± 0.6	1	2×10^{-1}	e
Current	fp	$\text{Br}^-, \text{N}_2\text{O}$	3.1 ± 0.6	6	10^{-3}	5.3.5
Current	fp	$\text{Br}^-, \text{N}_2\text{O}$	4.4 ± 1	6	10^{-1}	5.3.5
Current	fp	$\text{Br}^-, \text{N}_2\text{O}$	7.0 ± 2	6	1.0	5.3.5
Current	fp	Br^-, Br_2	5.3 ± 0.8	1	10^{-1}	5.3.7
Current	fp	$\text{Br}^-, \text{H}_2\text{O}_2$	5.5 ± 1	1	10^{-1}	5.3.8
Current	fp	FeBr^{2+}	5.2 ± 0.8	1	10^{-1}	5.3.9
Current	pr	$\text{Br}^-, \text{N}_2\text{O}$	3.3 ± 0.6	6	10^{-3}	4.7.3

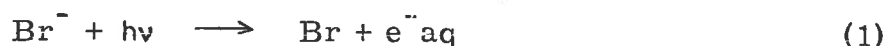
*Method

pr = pulse radiolysis

fp = flash photolysis

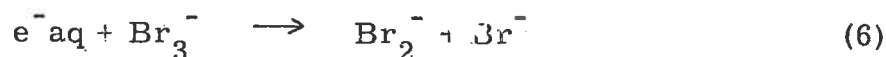
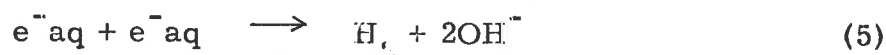
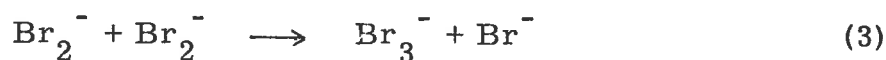
#References

- (a) Sutton, Adams, Boag and Michael (1965)
- (b) Cercek, Ebert, Gilbert and Swallow (1965)
- (c) Matheson, Mulac, Weeks and Rabani (1966)
- (d) Langmuir and Hayon (1967)
- (e) Malone and Endicott (1972)

5.3.1 Deaerated neutral bromide solution

Langmuir and Hayon (1967) suggest that flash photolysis of dilute aqueous bromide solutions produces Br_2^- decaying with a second order rate constant of $3.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. Attempts to reproduce this result were unsuccessful. In the absence of any added electron scavengers Br_2^- decayed by poor second order kinetics with a rate constant of about $1.2 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$.

Matheson, Mulac, Weeks and Rabani (1966) also found initial curvature (extending over 500 μs) in second order decay plots of Br_2^- from deaerated bromide solution. They attributed this to the reaction of aquated electrons with the Br_2^- radical anions ($k_4 \sim 1.3 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$)



A computer fit of our results using the above scheme gave $k_4 = (1.0 \pm 0.4) \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ in agreement with that of Matheson et. al.

5.3.2 Aerated neutral bromide solutions

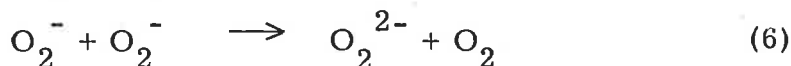
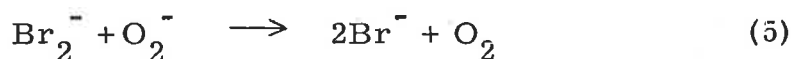
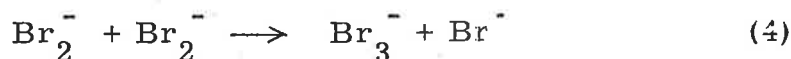
Oxygen reacts rapidly with aquated electrons and hydrogen atoms to produce hydroperoxy radicals (HO_2) or their conjugate base peroxy radical anions (O_2^-) - see 4.3.5



The pK of HO_2 is about 4.9 (Behar, Czapski, Rabani, Dorfman and Schwarz, 1970) so that above pH5, O_2^- predominates.



The decay of Br_2^- was poor second order with a rate constant of $(9 \pm 3) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.



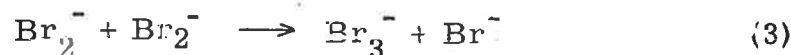
Computer fitting of the data gave $k_5 = (6 \pm 3) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. The value, as might be expected, is close to that obtained for the rate constant of the $(\text{Br}_2^-, \text{HO}_2)$ reaction (see 5.3.4)

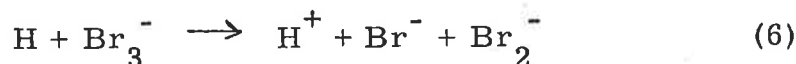
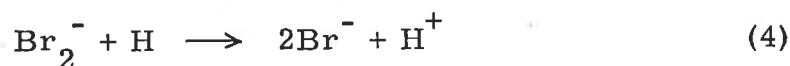
5.3.3 Acidified deaerated bromide solution

Aquated electrons produced in the photolysis of bromide ion are rapidly scavenged by acid (see 4.3.1)



The hydrogen atoms produced also react with Br_2^- (Sutton, Adams, Boag and Michael, 1965) which decays, in our experiments, by a poor second order process with $2k \sim 9 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. The decay can be analysed in terms of the following reactions.





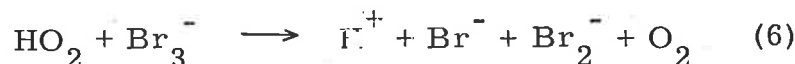
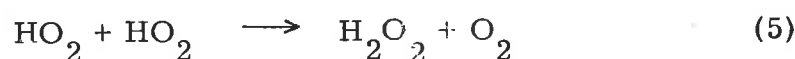
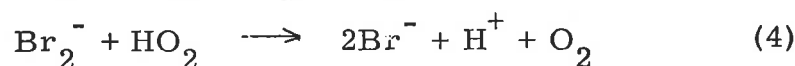
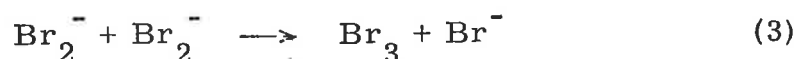
The best value of k_4 is $(7 \pm 3) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

5.3.4 Acidified aerated bromide solution

In aerated acidic solutions ($\text{pH} < 4$) oxygen scavengers hydrogen atoms to form hydroperoxy radicals (see 5.3.2)



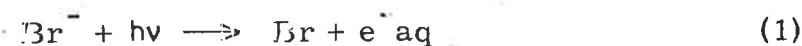
Decay of Br_2^- is poor second order with a rate constant, $2k$, of $(8 \pm 3) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. The reaction scheme can be written,

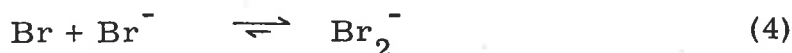
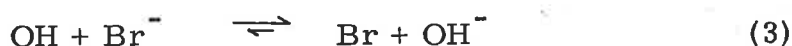
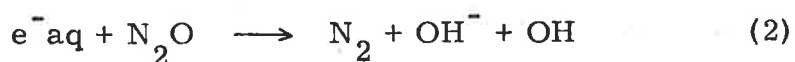


A computer fit of the rate of decay of Br_2^- in the first flash on a particular solution gave $k_4 = (4 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in reasonable agreement with values of (3.8) and $(1.6 \pm 0.5) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ obtained by Sutton, Adams, Boag and Michael (1965) and Cercek, Ebert, Gilbert and Swallow (1965) respectively.

5.3.5 Nitrous oxide saturated bromide solution

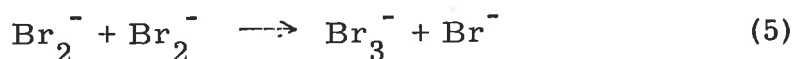
Nitrous oxide converts aquated electrons to hydroxyl radicals (see 4.3.2). In the presence of excess bromide hydroxyl radicals react to form bromide radical anions.





The stoichiometry of the primary process (1) suggests that addition of nitrous oxide to a deaerated bromide solution should exactly double the yield of Br_2^- if nitrous oxide has no effect on the amount of light absorbed, the quantum efficiency or the amount of geminate recombination. As shown in Table 5.3B, within the limits of experimental error a doubling is observed at all bromide concentrations.

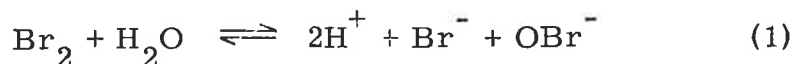
In nitrous oxide saturated neutral solutions the decay of Br_2^- is good second order with a rate constant that increases as the bromide concentration increases.



The values in Table 5.3B are in good agreement with literature values for the disproportionation rate constant (see Table 5.3A). The change in rate constant with bromide concentration can be attributed to the effect of changing ionic strength of the solutions. The variation is in reasonable agreement with that expected for a reactant charge produce of +1, supporting the proposition that the reaction occurs between singly charged ions of like sign.

5.3.6 Neutral aqueous bromine solution

In aqueous solution bromine is hydrolysed. (Pink, 1970)



Flash photolysis of bromine solutions containing $10^{-3} \text{ mol l}^{-1}$ bromide produces some transient but the decay is very rapid and mixed first and second order. It is probable that not only Br_2 is being photolysed but also hypobromite (Amichai and Treinin, 1969; Amichai, Czapski and Treinin, 1969). The increased rate of decay of Br_2^- may be due

Table 5.3B

$[\text{Br}^-]$ (mol l ⁻¹)	$[\text{Br}_2^-] \text{N}_2\text{O}$ (mol l ⁻¹)	$[\text{Br}_2^-] \text{N}_2\text{O} / [\text{Br}_2^-]^\circ \neq$	$2k_5 \times 10^{-9*}$ (l mol ⁻¹ s ⁻¹)
10 ⁻³	$(1.8 \pm 0.2) \times 10^{-6}$	1.9 ± 0.4	3.2 ± 0.1
10 ⁻¹	$(4.9 \pm 0.5) \times 10^{-6}$	2.0 ± 0.4	4.4 ± 0.3
1.0	$(1.6 \pm 0.4) \times 10^{-6}$	1.6 ± 0.6	7.0 ± 1.0

Notes:

$\neq [\text{Br}_2^-]^\circ$ is the yield of Br_2^- produced in a similar solution without N_2O

* Errors stated are reproducibilities they do not include 20% error in $\epsilon_{\text{Br}_2^-}$

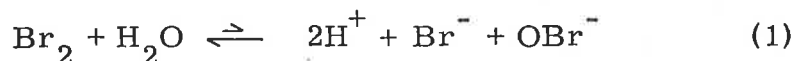
to reaction with OBr^- .



No rate measurements were made in this system.

5.3.7 Acidified bromine/bromide solution

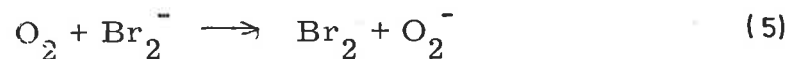
Acid and bromide suppress the hydrolysis of bromine with the subsequent formation of the tribromide ion. (Pink, 1970).



Br_2^- is formed in the flash photolysis of this solution. (See 1.4.3)



Decay of Br_2^- in this solution (pH 1 and 0.2 mol l^{-1} ionic strength) is excellent second order with a rate constant at 25° of $(5.3 \pm 0.8) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, in good agreement with literature values. (Table 5.3A). No change was observed upon deaeration or oxygenation of the solution. It is concluded that if oxygen does react with Br_2^- its rate constant is insignificantly small ($k_5 < 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$)

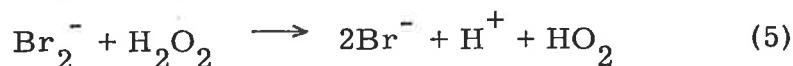
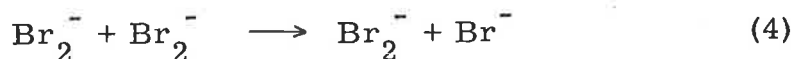


5.3.8 Hydrogen peroxide/bromide solution

Good yields of Br_2^- are formed in the flash photolysis of neutral or acidic solutions of bromide ion and hydrogen peroxide (see 1.4.4)

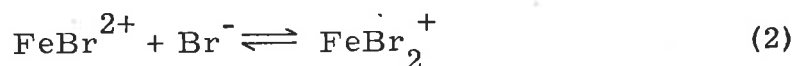
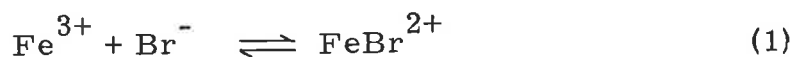


At low concentrations of hydrogen peroxide ($\sim 10^{-3} \text{ mol l}^{-1}$) the decay of Br_2^- is good second order with a rate constant, $2k_4$, of $(5.5 \pm 1) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ at $22 \pm 2^\circ \text{C}$ and 0.2 mol l^{-1} ionic strength. This is in reasonable agreement with literature values and values obtained in other systems (see Table 5.3A). At higher concentrations of H_2O_2 the fit of the decay of Br_2^- to a second order rate law becomes less good and a trend towards first order is apparent. The results can be analysed in terms of a relatively slow ($k_5 \sim 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$) reaction of hydrogen peroxide with Br_2^- competing with the disproportionation reaction (4).

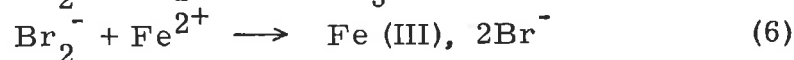
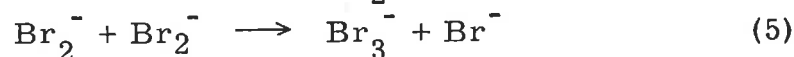
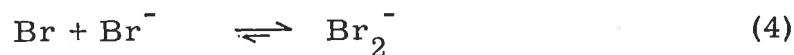
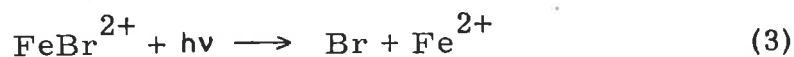


5.3.9 Acidified ferric bromide solution

In aqueous solution bromide and ferric ions form weak inner sphere complexes.



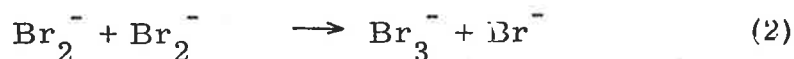
Photolysis of these complexes in the LMCT band leads to production of Br_2^- and aquated ferrous ions in equal concentration (see 1.4.2). The decay of Br_2^- is good second order over two half lives with a rate constant, $2k_5$, at 25°C and 0.2 mol l^{-1} ionic strength of $(5.2 \pm 0.8) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in good agreement with that measured in other systems (see Table 5.3A).



The reaction of ferrous with Br_2^- (6), does not interfere at these extremely low ferrous concentrations ($\sim 5 \times 10^{-6} \text{ mol l}^{-1}$), because as later results (13. 1. 1) show the rate constant, k_6 , is $\sim 2 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$, 10^3 times slower than the disproportionation reaction.

5.3.10 Temperature dependence of Br_2^- disproportionation rate constant

A solution of bromine with excess bromide and acid was used to generate Br_2^- for a study of the temperature dependence of the disproportionation rate constant (cf Section 5.3.7). No permanent changes were observed in the system at 366 nm.



The following parameters were obtained:

$$\Delta H_2^\ddagger = 11 \pm 2 \quad \text{kJ mol}^{-1}$$

$$\Delta S_2^\ddagger = -22 \pm 4 \quad \text{J mol}^{-1} \text{K}^{-1}$$

$$2k_2 (25^\circ \text{C}) = (5.3 \pm 0.8) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$$

5.3.11 Summary

See Table 5.3C

Table 5.3C

Derived Rate Constants

Reaction	Section	Ionic Strength (mol l ⁻¹)	Rate Constant x 10 ⁻⁹ (l mol ⁻¹ s ⁻¹)	Lit. Value x 10 ⁻⁹ (l mol ⁻¹ s ⁻¹)
Br ₂ ⁻ + Br ₂ ⁻	5.3.5	10 ⁻³	3.1 ± 0.6*	3.3 ^a
	4.7.3	10 ⁻³	3.3 ± 0.6	
	5.3.7			
Br ₂ ⁻ + Br ₂ ⁻	5.3.8	0.2	5.3 ± 0.8*	-
	5.3.9			
Br ₂ ⁻ + e ⁻ aq	5.3.1	10 ⁻¹	10 ± 4	13 ^b
	4.7.1	10 ⁻²	8 ± 4	
Br ₂ ⁻ + H	5.3.3	10 ⁻¹	7 ± 3	3.3 ^c
	4.7.1	10 ⁻²	5 ± 2	
Br ₂ ⁻ + O ₂ ⁻	5.3.2	10 ⁻¹	6 ± 3	-
Br ₂ ⁻ + HO ₂	5.3.4	10 ⁻¹	4 ± 2	3 ^{c, d}
Br ₂ ⁻ + H ₂ O ₂	5.3.8	0.2	10 ⁻⁴	-

Notes

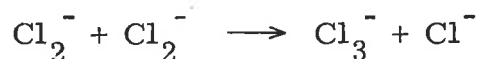
*Value quoted is 2k

References Table 5.3C

- (a) See References to Table 5.3A
- (b) Matheson, Mulac, Weeks and Rabani (1966)
- (c) Sutton, Adams, Boag, and Michael (1965)
- (d) Cercek, Ebert, Keene and Swallow (1965)

5.4 DECAY OF Cl_2^-

Grossweiner and Matheson (1957) observed Cl_2^- in the flash photolysis of chloride solutions but did not measure the rate of decay. In 1967 Langmuir and Hayon found a second order decay of Cl_2^- in solutions of sodium chloride and mercuric chloride complexes. They attributed this to the disproportionation reaction,



with a rate constant of $(1.3 \pm 0.2) \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. We believe that a more complex reaction scheme is involved. Malone and Endicott (1972) measured the rate of decay of Cl_2^- in nitrous oxide saturated chloride solution at pH 1. At this pH nitrous oxide is not an effective electron scavenger (see 4.3.1, 4.3.2) and hydrogen atoms present in their solution may complicate the decay of Cl_2^- (see 5.4.3). They also observed the decay of Cl_2^- in a solution of Co(trans [14]diene) Cl_2^+ but found significantly curved second order plots. The literature to this time does not appear to contain an authoritative report of the Cl_2^- disproportionation rate constant. Table 5.4A lists our values and compares them with previously published values.

5.4.1 Neutral deaerated chloride solution

Cl atoms are produced directly by the primary photochemical process in the flash photolysis of chloride solutions (see 1.4.1)

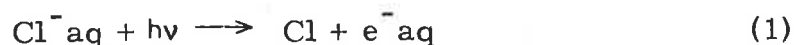
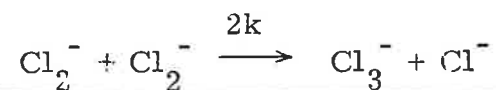


Table 5.4A



Year	Method*	System	$2k \times 10^{-9}$ ($\text{l mol}^{-1} \text{s}^{-1}$)	pH	$[\text{Cl}^-]$ (mol l^{-1})	Ref [#]
1967	fp	Cl^-	15.1 ± 1	6	0.5	a
1967	fp	Cl^-	13.8 ± 2	1	0.5	a
1967	fp	HgCl_4^{2-}	12.5 ± 1	6	0.5	a
1967	fp	HgCl_4^{2-}	15.0 ± 1	1	0.5	a
1972	fp	$\text{Cl}^-, \text{N}_2\text{O}$	8.4 ± 2	1	1.0	b
1972	fp	$\text{Co}(\text{A}_4)\text{Cl}_2^+$	8.2 ± 4	1	1.0	b
Current	fp	$\text{Cl}^-, \text{N}_2\text{O}$	7.0 ± 1	4	0.5	5.4.5
Current	fp	Cl^-, Cl_2	6.0 ± 1	1	0.5	5.4.7
Current	fp	Cl^-, Cl_2	5.5 ± 0.5	1	0.1	5.4.7
Current	fp	$\text{Cl}^-, \text{H}_2\text{O}_2$	5.5 ± 1	1	0.1	5.4.8
Current	fp	FeCl^{2+}	5.5 ± 0.8	1	0.1	5.4.9
Current	pr	$\text{Cl}^-, \text{N}_2\text{O}$	6.0 ± 2	4	0.5	4.8.3

*Method

pr = pulse radiolysis

fp = flash photolysis

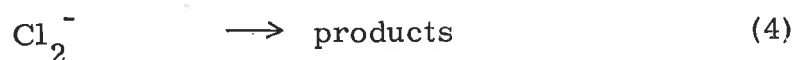
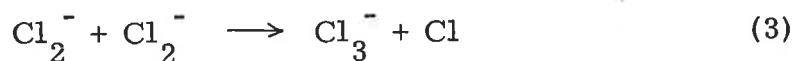
#References

(a) Langmuir and Hayon (1967)

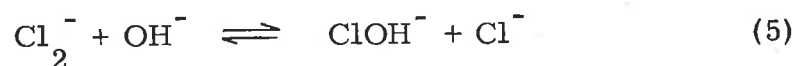
(b) Malone and Endicott (1972)

The low efficiency of the photolyzing flash at wavelengths $< 200\text{nm}$ where Cl^- is photoactive is responsible for the small ($\sim 10^{-7} \text{ mol l}^{-1}$) yields of Cl_2^- with dilute chloride solutions. Table 5.4B lists the yield of Cl_2^- from flash photolyzed chloride solution as a function of chloride concentration.

The decay of Cl_2^- in dilute neutral deaerated chloride solution approaches first order with a rate constant of $\sim 1.5 \times 10^3 \text{ s}^{-1}$, depending somewhat on the concentration of chloride. The fit is not good and it is probable that the decay of Cl_2^- is a mixture of first and second order processes.



Cl_2^- is in equilibrium with other radical species Cl , ClOH^- and OH (see 4.5)

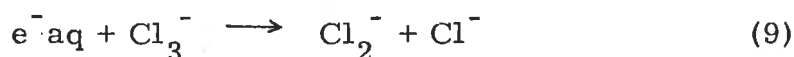
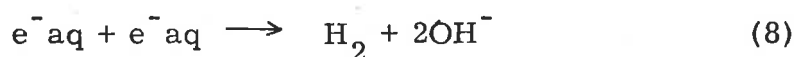
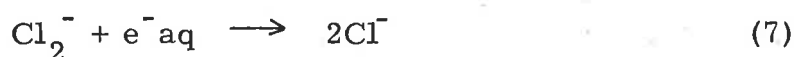
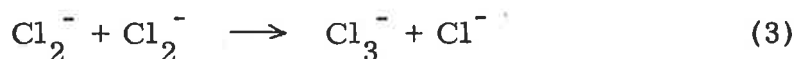


At pH 7 the equilibria lie almost completely in favour of ClOH^- and OH . In the absence of any other decay reactions such as (3), Cl_2^- would equilibrate by first order processes. The observed first order decay is probably due to reaction (5). The rate constant k_5 must therefore be about $10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ to obtain the observed first order rate constant at $[\text{OH}^-] = 10^{-7} \text{ mol l}^{-1}$. A reasonable estimate of the second order component could not be made.

Langmuir and Hayon (1967) studied the decay of Cl_2^- in neutral 0.5 mol l^{-1} chloride solution and observed a second order decay with a rate constant attributed to $2k_3$ of $1.5 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$.

Under identical conditions we observed a similar second order process with rate constant $1.8 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. The fit of the decay to a second order plot is poor, with the observed rate constant decreasing

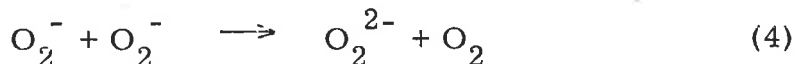
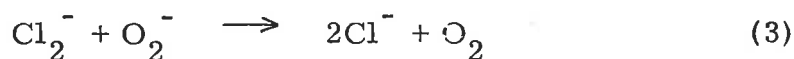
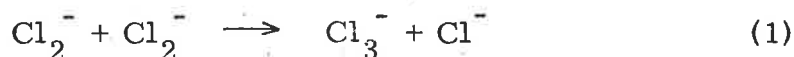
as the reaction proceeds. Results in the analogous bromide system were interpreted in terms of a concurrent reaction with e^-_{aq} .



Computer simulation of the Cl_2^- decay curve using the above scheme gives a satisfactory fit to the experimental data with $k_7 = (1.5 \pm 0.5) \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. It is probable that the second order decay of Cl_2^- observed by Langmuir and Hayon (1967) is not solely due to reaction (3) but involves reactions (7) to (9).

5.4.2 Neutral aerated chloride solution

To maximize the yield of Cl_2^- and minimize the effect of the first order equilibration reactions, only 0.5 mol l^{-1} chloride was investigated in neutral aerated solution. Aqueated electrons are rapidly scavenged by oxygen in aerated solution (see 4.3.5). The resulting peroxy radicals may react with Cl_2^- .

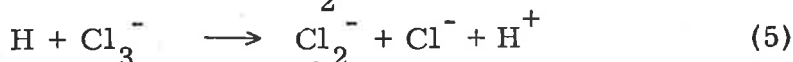
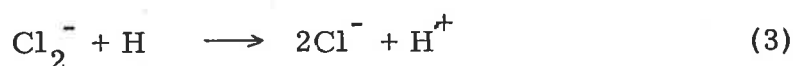


The decay of Cl_2^- in neutral aerated solution was poor second order with a rate constant of $(1.8 \pm 0.5) \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. Computer fitting of the experimental decay curve was achieved with $k_3 = (1.2 \pm 0.5) \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$.

5.4.3 Acidified deaerated chloride solution

The decay of Cl_2^- in acidified deaerated solution was second

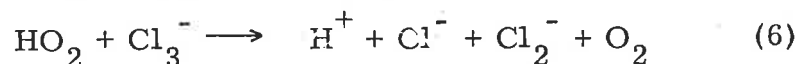
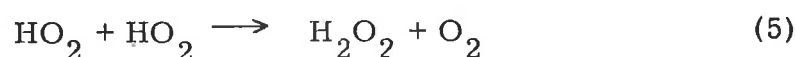
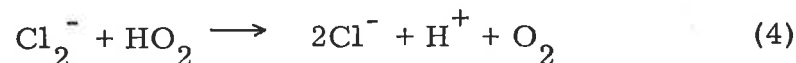
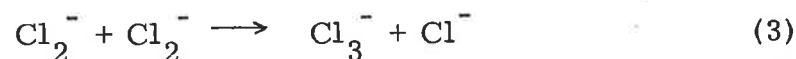
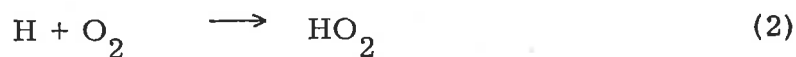
order with significant initial curvature, similar to that observed in the pulse radiolysis of deaerated acidified chloride.



The Cl_2^{-} decay was adequately computer fitted by the above scheme with $2k_2 = 6 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_3 = (1.0 \pm 0.4) \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. At pH 2 the rate of decay was almost independent of chloride concentrations above $10^{-2} \text{ mol l}^{-1}$.

5.4.4 Acidified aerated chloride solution

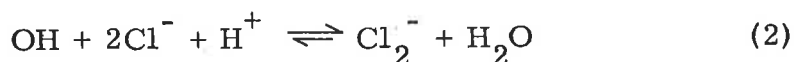
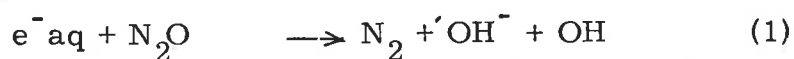
In acidified aerated solution the decay of Cl_2^{-} was poor second order. The second order plot showed the typical upward curvature experienced when the other reactive radical (in this case HO_2) decays slower than the halogen radical anion. After considerable reaction has taken place $[HO_2] \gg [Cl_2^{-}]$, and the plots approach first order. The decay of Cl_2^{-} can be fitted by the scheme,



The best value of k_4 was estimated as $(5 \pm 3) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

5.4.5 Nitrous oxide saturated chloride solutions

Above pH 4 nitrous oxide scavenges aquated electrons to produce hydroxyl radicals (see 4.3.2). Depending upon the acid and chloride concentrations hydroxyl radicals may react with chloride to form Cl_2^- .



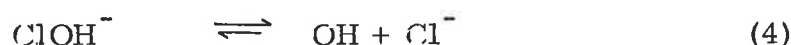
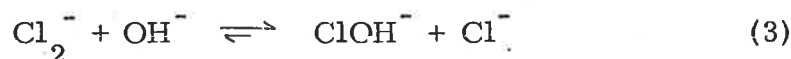
If reaction (2) is complete the yield of Cl_2^- should be twice that in a nitrous oxide free solution. Table 5.4B lists the Cl_2^- yields under various chloride concentrations and acidities with and without N_2O .

Table 5.4B

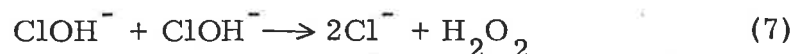
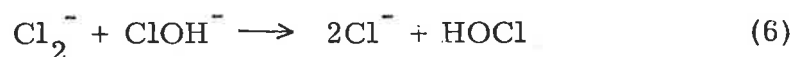
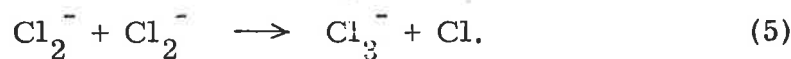
$[\text{Cl}^-]$ (mol l ⁻¹)	pH	$[\text{N}_2\text{O}]$ (mol l ⁻¹)	Yield Cl_2^- (mol l ⁻¹)
10 ⁻³	7	0	$(3.0 \pm 0.5) \times 10^{-8}$
10 ⁻³	4	0	$(2.8 \pm 0.5) \times 10^{-8}$
10 ⁻³	7	10 ⁻²	$(2.5 \pm 0.5) \times 10^{-8}$
10 ⁻³	4	10 ⁻²	$(3.0 \pm 0.5) \times 10^{-8}$
10 ⁻²	7	0	$(5.5 \pm 1) \times 10^{-8}$
10 ⁻²	7	10 ⁻²	$(7 \pm 1) \times 10^{-8}$
0.5	7	0	$(6.1 \pm 0.5) \times 10^{-7}$
0.5	4	0	$(6.2 \pm 0.5) \times 10^{-7}$
0.5	7	10 ⁻²	$(6.0 \pm 0.5) \times 10^{-7}$
0.5	4	10 ⁻²	$(1.2 \pm 0.2) \times 10^{-6}$

It can be seen that only at pH 4 with high chloride concentrations is the expected doubling realized. This implies that under all other conditions radicals other than Cl_2^- , namely OH and ClOH^- , will be present. These may complicate the decay of Cl_2^- .

In N_2O saturated dilute chloride solution (10^{-3} - 10^{-2} mol l^{-1}) at pH 7 and pH 4 the decay of Cl_2^- approaches first order with a rate constant of between 1.5 and $2.0 \times 10^3 \text{ s}^{-1}$, depending only slightly on chloride concentration. The first order decay is due to the equilibration between Cl_2^- and ClOH^- or OH due to the formation of Cl_2^- in excess of equilibrium concentrations in the primary photolytic step.



The decay of Cl_2^- in N_2O saturated 0.5 mol l^{-1} chloride solution at pH 7 is roughly second order with a rate constant of $(9 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. Slight upward curvature is observed in the second order plots suggesting that reaction with another more slowly decaying radical is occurring concurrently with the disproportionation reaction (5). The only other radical species of significant concentration under these conditions is ClOH^- .



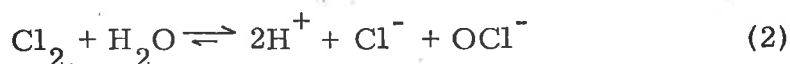
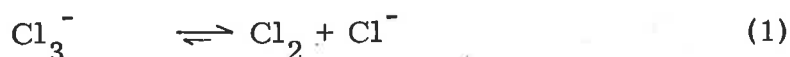
The results suggest that $k_7 < k_5 \sim k_6$ but computer simulation with three unknown rate constants is unreliable.

At pH 4 in N_2O saturated 0.5 mol l^{-1} chloride solution, Cl_2^- is the only significant radical. The decay of Cl_2^- is good second order over at least 2 half lives with a rate constant of $(7 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, attributed to the disproportionation reaction (5). Allowing for ionic

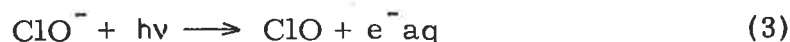
strength differences this value is in reasonable agreement with other measured values of the disproportionation rate constant (see Table 5.4A).

5.4.6 Neutral aqueous chlorine solution

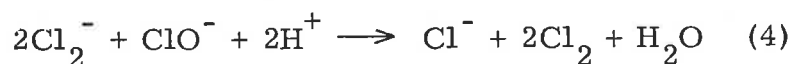
Even at high (0.5 mol l^{-1}) chloride concentrations, chlorine is extensively hydrolysed in neutral aqueous solution (Eigen and Kustin, 1962).



The presence of hypochlorite ions complicates the system by producing other radicals on photolysis (Treinin, 1970).



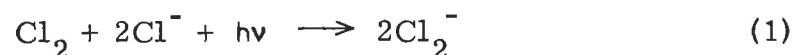
and directly reacting with Cl_2^-



Moderate ($\sim 2 \times 10^{-6} \text{ mol l}^{-1}$) yields of some transient, presumably Cl_2^- , were produced by flash photolysis of neutral aqueous chlorine solutions. The decay of this transient was intermediate between first and second order. No further rate measurements were made in this system.

5.4.7 Acidified chlorine/chloride solution

Hydrolysis of chlorine can be suppressed by addition of chloride and acid. In 0.1 mol l^{-1} chloride at pH 1 approximately 4% of the total chlorine is hydrolysed and the small concentration of HOCl formed is apparently negligible. Flash photolysis of chlorine solution produces Cl_2^- free of other radicals (see 1.4.3)



In this system the decay of Cl_2^- is good second order over several half lives with a rate constant $2k_1$ of $(5.5 \pm 0.5) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$

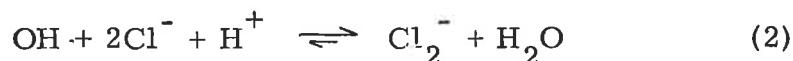
in $0.1 \text{ mol l}^{-1} \text{ Cl}^-$ and $(6 \pm 1) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in $0.5 \text{ mol l}^{-1} [\text{Cl}]$. These values are in good agreement with other estimates of $2k_1$ in systems where Cl_2^- is the only significant radical (see Table 5.4A).

5.4.8 Acidified hydrogen peroxide/chloride solution

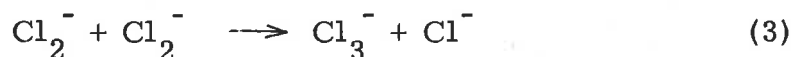
Hydroxyl radicals are produced by flash photolysis of dilute ($\sim 10^{-3} \text{ mol l}^{-1}$) hydrogen peroxide solution (see 1.4.4).



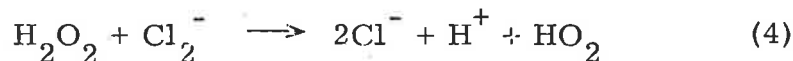
In acid chloride solution, Cl_2^- radical anions are subsequently formed.



The decay of Cl_2^- is good second order over at least two half lives with a rate constant, $2k_3$, of $(5.5 \pm 1) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in good agreement with other values of the disproportionation rate constant (see Table 5.4A).



A single experiment at $10^{-1} \text{ mol l}^{-1}$ hydrogen peroxide suggested that at these concentrations reaction (4) was significant, k_4 can be estimated as $2 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$.

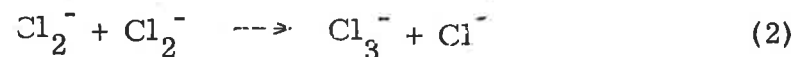


5.4.9 Acidified ferric chloride solution

Ligand to metal charge transfer in chloroiron (III) ions produces Cl_2^- and ferrous ions (1.4.2).

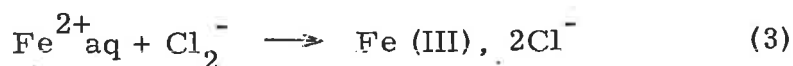


The decay of Cl_2^- is reasonable second order over almost two half lives but due to interfering absorbance by $\text{FeCl}^{2+}_{\text{aq}}$ at 366 nm, appears to tend towards first order after two half lives.



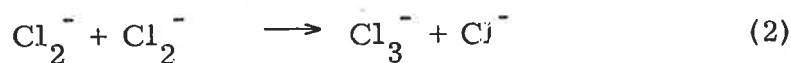
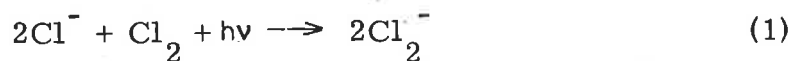
The disproportionation rate constant $2k_2$, can be calculated as $(5.5 \pm 0.8) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in good agreement with other values (see Table 5.4A). Computer simulation of the absorbance against time curve to take account of the absorbance due to $\text{FeCl}^{2+}_{\text{aq}}$ provides a better fit to the experimental curve than either simple first or second order reactions.

The reaction of $\text{Fe}^{2+}_{\text{aq}}$, formed in micromolar concentrations in the primary step, with Cl_2^- can be neglected because as later results (13.1.1) show $k_3 \approx 1.4 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, over 10^2 times slower than the disproportionation reaction (2).



5.4.10 Temperature dependence of Cl_2^- disproportionation rate constant

A solution of chlorine ($\sim 10^{-2} \text{ mol l}^{-1}$) in 0.1 mol l^{-1} chloride and 0.1 mol l^{-1} perchloric acid was used to study the effect of temperature on the disproportionation rate constant, $2k_2$. The photolysis flash was restricted to wavelengths above 220 nm by a quartz filter. No permanent changes were observed at 366 nm (see 5.4.7).



The following parameters were obtained

$$\Delta H^\ddagger = 10 \pm 2 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = 25 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$2k_2 (25^\circ \text{C}) = (5.5 \pm 0.5) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1} \quad (I = 0.2 \text{ mol l}^{-1})$$

5.4.11 Summary

See Table 5.4C

Table 5.4C

Derived Rate Constants

Reaction	Section	Ionic Strength (mol l ⁻¹)	Rate Constant x 10 ⁻⁹ (l mol ⁻¹ s ⁻¹)	Lit. Value x 10 ⁻⁹ (l mol ⁻¹ s ⁻¹)
$\text{Cl}_2^- + \text{Cl}_2^-$	5.4.7	0.2	$5.5 \pm 0.5^*$	12^a
	5.4.8			
	5.4.9			
$\text{Cl}_2^- + \text{Cl}_2^-$	4.8.3	0.5	$6 \pm 2^*$	12^a
$\text{Cl}_2^- + e^-_{\text{aq}}$	5.4.1	0.5	15 ± 5	-
	4.8.1	0.5	10 ± 5	-
$\text{Cl}_2^- + \text{H}$	5.4.3	0.1	10 ± 4	-
	4.8.2	0.02	10 ± 5	-
$\text{Cl}_2^- + \text{O}_2^-$	5.4.2	0.5	12 ± 5	-
$\text{Cl}_2^- + \text{HO}_2$	5.4.4	0.5	5 ± 3	-

Notes

*Value quoted is 2k

References

(a) Langmuir and Hayon (1967)

5.5 DECAy OF I_2^-

The first direct observation of a reaction of halogen radical anions was by Stottlemeyer (1953) when he observed second order decay of a transient species, proposed to be I_2^- , in flash photolysed iodide/iodine solutions. Without knowledge of the extinction coefficient of the species involved the absolute second order rate constant could not be obtained. Grossweiner and Matheson (1957) performed a detailed study of the disappearance of I_2^- from iodide and tri-iodide solutions as a function of iodide concentration and pH. They obtained a second order rate constant which depended upon iodide concentration below $10^{-3} \text{ mol l}^{-1}$. The rate constant was pH independent. They attributed the iodide ion dependence to three simultaneous reactions.

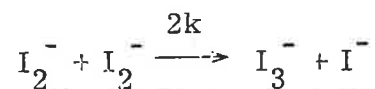


All our experiments were performed with $[I^-] \geq 10^{-2} \text{ mol l}^{-1}$; under these conditions equilibrium (4) is 1000:1 in favour of I_2^- (Baxendale and Bevan, 1969), and reaction (3) is the only one of importance. Malone and Endicott (1972) in their study of reactions of halogen radical anions with macrocyclic Co (II) complexes reported values of the disproportionation rate constant of I_2^- produced from a variety of systems. Their results show wide variation. Literature values and our values, under various conditions, for the disproportionation rate constant $2k_3$ are given in Table 5.5A.

5.5.1 Deaerated iodine/iodide solution

Unlike chlorine or bromine, iodine is not extensively hydrolysed in neutral aqueous solution.

Table 5.5A



Year	Method*	System	$2k \times 10^{-9}$ ($\text{l mol}^{-1} \text{s}^{-1}$)	pH	$[\text{I}^-]$ (mol l^{-1})	Ref
1953	fp	I_3^-	7	?	?	a
1957	fp	I^-	7.7 ± 1.5	1-6	10^{-3}	b
1957	fp	I_3^-	9 ± 3	4-6	0.1	b
1972	fp	I^-	7 ± 1	3	10^{-2}	c
1972	fp	$\text{CoA}_6^{3+} \cdot \text{I}^-$	3.5 ± 0.6	3	10^{-2}	c
1972	fp	$\text{CoA}_5 \text{I}^{2+}$	5.4 ± 2	1	10^{-3}	c
Current	fp	I^-	9.3 ± 3	6	2×10^{-2}	5.5.3
Current	fp	I_3^-	8.7 ± 2	6	2×10^{-2}	5.5.1
Current	fp	I_3^-	9.2 ± 2	4 ⁷	4×10^{-2}	5.5.6
Current	pr	$\text{I}^-, \text{N}_2\text{O}$	8.0 ± 1	6	10^{-2}	4.9.1

Notes

* fp = flash photolysis

pr = pulse radiolysis

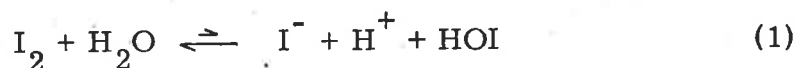
≠ 25°C

References

(a) Stottlemeyer (1953)

(c) Malone and Endicott (1972)

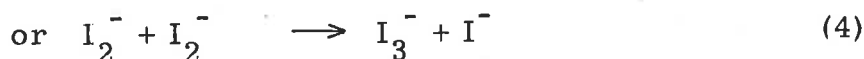
(b) Grossweiner and Matheson (1957)



The minimum iodide concentration used in our experiments was $2 \times 10^{-2} \text{ mol l}^{-1}$. Under these conditions reaction (1) is effectively 100% to the left. It is not necessary to work at low pH to effectively suppress hydrolysis.

Figure 5.5A shows the absorption spectra of I_2^- and I_3^- in the range 300 - 500 nm. Where the curves cross (i. e. $\sim 365 \text{ nm}$),

$\epsilon_{\text{I}_2^-} = \frac{1}{2} \epsilon_{\text{I}_3^-}$ and a process such as



will show no absorbance change.

Flash photolysis of a deaerated tri-iodide ion solution at 366 nm shows very little transient or permanent change in absorbance despite the large changes observed at other wavelengths. This suggests that in this system reactions (3) and (4) adequately describe the changes produced by photolysis. At wavelengths above 365 nm an initial increase in optical density due to I_2^- formation followed by a decrease to the initial value due to reaction (4) is observed. The decay of I_2^- follows good second order kinetics with a rate constant of $(9.2 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in good agreement with the value of $(9 \pm 3) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ reported by Grossweiner and Matheson under similar conditions.

Observation at 313 nm where $\epsilon_{\text{I}_2^-} < \frac{1}{2} \epsilon_{\text{I}_3^-}$ shows an initial decrease in absorbance due to removal of I_3^- followed by an increase as I_3^- is reformed by reaction (4). The rate of I_3^- formation exhibits good second order kinetics with a rate constant of $(8.0 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in reasonable agreement with the rate of decay of I_2^- .

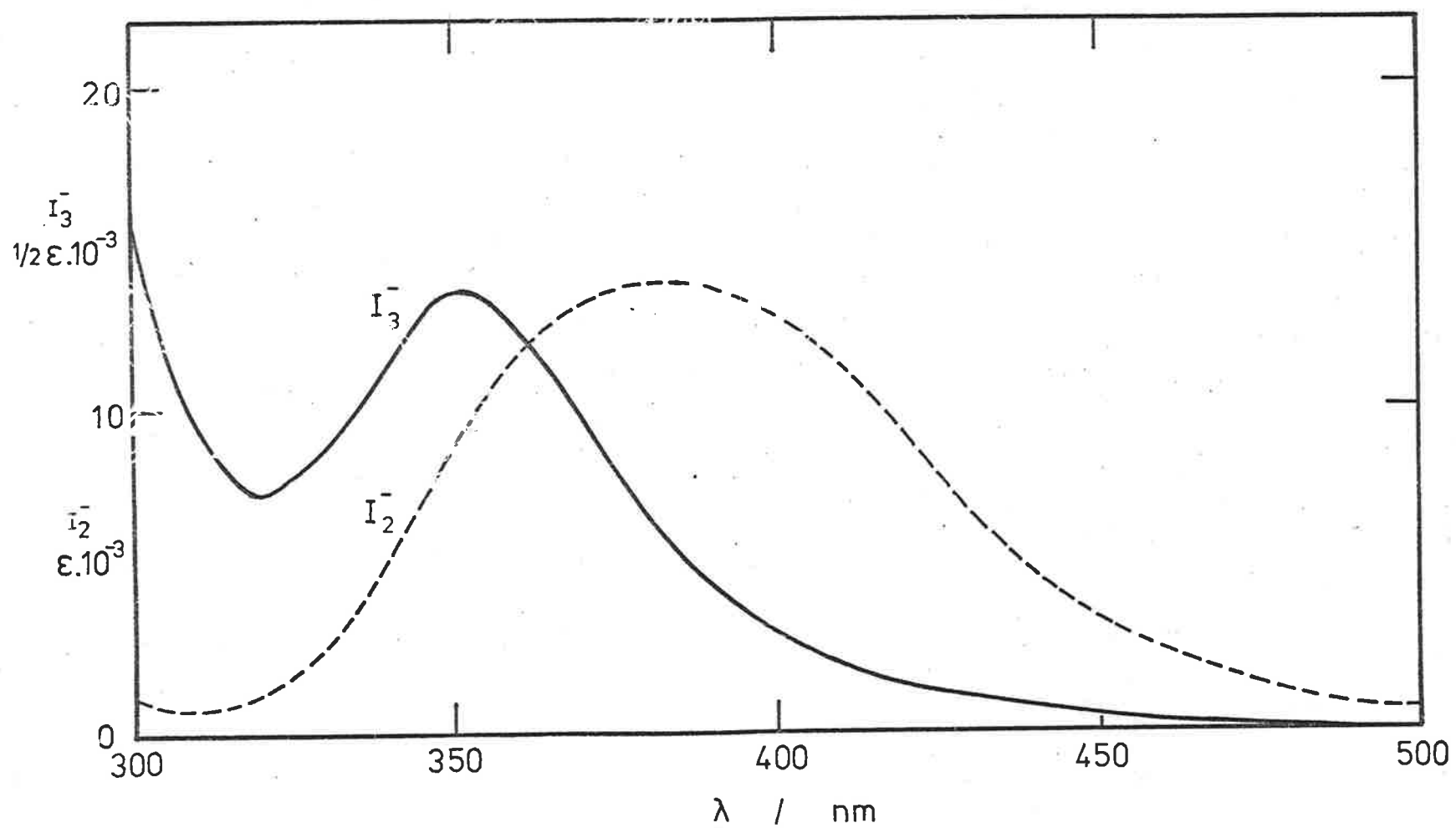


Fig. 5.5A Spectra I_3^- , I_2^-

5.5.2 Aerated iodine/iodide solution

Decay of I_2^- at 405 nm in flash photolysed aerated iodine solution exhibits moderately good second order kinetics over the first half life but subsequently tends towards first order, behaviour typical of a situation in which first and second order reactions compete for removal of the transient. Analysis of the decay curves using a second order component, $2k_1$, of $8.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ gives a good fit of the data with a first order component of $(4 \pm 1) \times 10^3 \text{ s}^{-1}$



Comparison with deaerated iodine solution suggests that the additional first order component is due to reaction of I_2^- with O_2 .



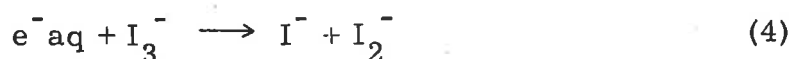
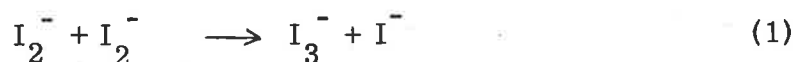
The concentration of oxygen in aerated water is about $2 \times 10^{-4} \text{ mol l}^{-2}$ so that a pseudo first order rate constant of $4 \times 10^3 \text{ s}^{-1}$ corresponds to an absolute second order rate constant of $2 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ for k_2 .

No reaction of Br_2^- or Cl_2^- with oxygen was observed ($k < 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$). Observation of reaction between I_2^- and oxygen is not surprising when the relative free energy changes for the reactions of X_2^- radical anions with O_2 are considered. Reaction (2) for I_2^- is at least 35 kJ mol^{-1} more exothermic than for Br_2^- or Cl_2^- (see Appendix 2.3). If the rate of reaction (2) is controlled solely by free energy considerations an acceleration of at least 10^5 times could be expected for I_2^- compared to Br_2^- or Cl_2^- . This is more than sufficient to account for the above observations.

5.5.3 Deaerated iodide solutions

Observation of the decay of I_2^- at 405 nm from deaerated iodide solution shows slight initial curvature in second order plots over about $150 \mu\text{s}$, followed by a good second order decay with a rate constant of $(9.3 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. The initial rapid decay is analogous

to that observed in deaerated neutral bromide and chloride solution (see 5.3.1, 5.4.1) and can be attributed to reaction of I_2^- with aquated electrons.

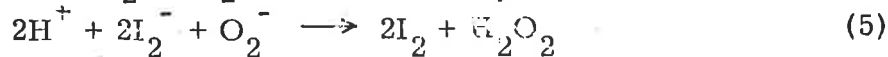
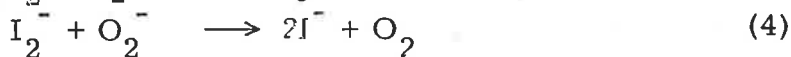
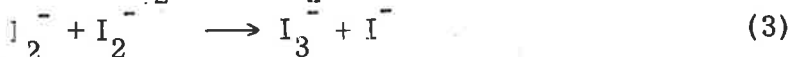
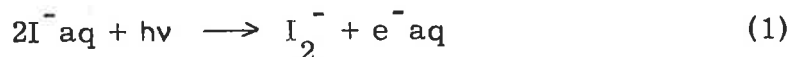


Analysis of the decay curve in terms of the above scheme gives $k_2 = (6 \pm 3) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

The yield of I_3^- observed at 405 nm is about 75% of that expected if all the I_2^- was converted to I_3^- by reaction (1). This is in qualitative agreement with the kinetic observation that reaction (1) is not the only one of importance, but reaction (2) must also be considered.

5.5.4 Aerated iodide solution

In aerated solution aquated electrons are rapidly scavenged by oxygen to form O_2^- (see 4.3.5). In aerated iodide solution second order plots of I_2^- decay show slight initial curvature over about 300 μs followed by a good second order process with rate constant, $2k_3$, of $(8 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. After about 1ms the decay tends towards first order in a similar manner to the decay of I_2^- in aerated iodine solution (see 5.5.2).

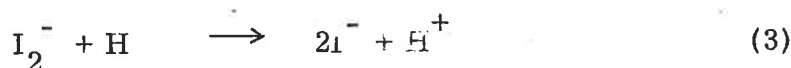
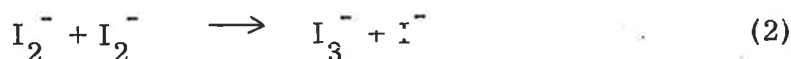


k_4 can be estimated as $(2 \pm 1) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

Our observations on the yield of I_3^- immediately after the decay of I_2^- are in complete accord with those of Grossweiner and Matheson (1957). It is found that the yield of I_3^- in aerated solution is about 25% higher than in deaerated solution, an observation which is undoubtedly due to the occurrence of reaction (5) with a 1:1 $\text{I}_2:\text{I}_2^-$ stoichiometry rather than the 2:1 stoichiometry of reaction (3).

5.5.5. Acidified deaerated iodide

The decay of I_2^- in acidified deaerated iodide solution is excellent second order. Aqueated electrons are rapidly scavenged by acid to form hydrogen atoms (see 4.3.1). The lack of initial curvature in the second order plots suggests that if reaction between H and I_2^- occurs its rate must be $< 2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ (compare 5.3.3 5.4.3).

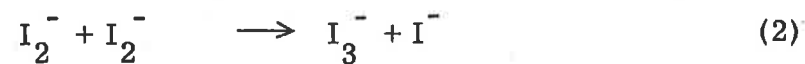
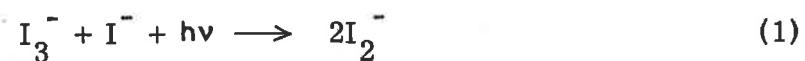


From the second order plots $2k_2$ was found to be $(8.9 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in excellent agreement with independently measured values. The low value of k_3 is in agreement with an estimate of $(1.8 \pm 0.8) \times 10^7 \text{ l mol s}^{-1}$ from photochemical methods by Dainton and Sills (1962).

5.5.6 Temperature dependence of I_2^- disproportionation rate constant

A deaerated solution of iodine ($\sim 10^{-5} \text{ mol l}^{-1}$) in iodine ($\sim 4 \times 10^{-2} \text{ mol l}^{-1}$) was used to study the disproportionation rate constant as a function of temperature. The photolysis flash was restricted to wavelengths above 270 nm by a pyrex filter. No permanent changes

were observed in the system at 405 nm (see 5.5.1)



The following parameters were obtained

$$\Delta H^\ddagger = 11 \pm 2 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = 12 \pm 6 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$2k_2 (25^\circ \text{C}) = (9.2 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$$

5.5.7 Summary

See Table 5.5B

Table 5.5B
Derived Rate Constants

Reaction	Section	Ionic Strength (mol l ⁻¹)	Rate Constant x 10 ⁻⁹ (l mol ⁻¹ s ⁻¹)	Lit. Value x 10 ⁻⁹ (l mol ⁻¹ s ⁻¹)
$I_2^- + I_2^-$	5.5.1	~ 0.04	$8.5 \pm 2^*$	7.5 ± 2^a
	5.5.3			
	5.5.5			
	5.5.6			
	4.9.1			
$I_2^- + e^-_{aq}$	5.5.3	0.02	6 ± 3	-
$I_2^- + H$	5.5.5	0.04	< 2	$1.8 \times 10^{-2}^b$
$I_2^- + O_2^-$	5.5.4	0.02	2 ± 1	-
$I_2^- + O_2$	5.5.2	0.02	$(2 \pm 1) \times 10^{-2}$	-

Notes

*Value quoted is 2k

References

(a) Grossweiner and Matheson (1957)

(b) Dainton and Sills (1961)

5.6 COMPARISON OF ACTIVATION PARAMETERS FOR X_2^- DISPROPORTIONATION

The upper limit for the rate of any reaction is determined by the rate at which the reactants can diffuse together. Theoretical calculations by Debye and Smoluchowski (see Caldin, 1964) suggest an upper limit of about $10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ for reaction between uncharged species. The predicted value of a diffusion controlled rate constant depends on both the charge product of the reactants (+1 for disproportionation of X_2^-) and to a lesser extent the size of the reacting species. For relatively large X_2^- radical anions the diffusion controlled rate constant is expected to be around $5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

The rate limiting step for a diffusion controlled reaction is the diffusion of the reactants; consequently the observed activation parameters refer to the process of diffusion. Theoretical calculations of the energy of activation for a diffusion controlled reaction give an approximate upper limit of 13 kJ mol^{-1} .

The rate constants and activation parameters for X_2^- disproportionation reactions are all close to the expected diffusion controlled limit. Although the rate constants at 25°C do not show a monotonic variation that might be expected from Cl_2^- to I_2^- , the activation parameters do show a small monotonic variation.

It is apparent that the disproportionation reactions of halogen radical anions are diffusion controlled.

Table 5.6A



Reaction	Section	Ionic Strength (mol l ⁻¹)	2k(25°C) × 10 ⁻⁹ (l mol ⁻¹ s ⁻¹)	ΔH [‡] (kJ mol ⁻¹)	ΔS [‡] (J mol ⁻¹ K ⁻¹)
Cl ₂ ⁻ + Cl ₂ ⁻	5.4.10	0.2	5.5 ± 0.8	10 ± 2	- 25 ± 6
Br ₂ ⁻ + Br ₂ ⁻	5.3.10	0.2	5.3 ± 0.8	11 ± 2	- 22 ± 6
I ₂ ⁻ + I ₂ ⁻	5.5.6	0.04	9.2 ± 2	11 ± 2	- 12 ± 6

PART II

REDOX REACTIONS

SECTION 11 - INTRODUCTION

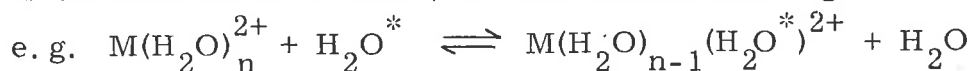
This thesis deals specifically with redox reactions between halogen radical anions and divalent first row transition metal ions. Electron transfer reactions of radicals with transition metal ions are discussed in 11.5 and 11.6. In sections 11.2, 11.3, and 11.4 redox reactions of metal complexes are used to illustrate the nature and observational consequences of "inner-sphere" and "outer-sphere" mechanisms. Substitution reactions of divalent first row transition metal ions are briefly discussed in 11.1 because of their particular relevance to inner-sphere electron transfer reactions.

11.1 SUBSTITUTION REACTIONS OF DIVALENT FIRST ROW TRANSITION METAL AQUO IONS

Substitution reactions of transition metal complexes have been the subject of numerous reviews (Langford & Gray, 1965; Eigen & Wilkins, 1965; Hewkin & Prince, 1970; Sutin, 1966; Hunt, 1971). No attempt at a comprehensive survey will be made, but reactions of particular interest, namely substitution reactions of divalent first row transition metal aquo complexes will be outlined. These reactions are typical of substitutions on labile metal complexes (Hewkin & Prince, 1970)

11.1.1 Solvent exchange

A fundamental substitution reaction for a solvated metal cation is substitution of solvent (i. e. the solvent exchange reaction)



For aquo metal cations this reaction can be followed by isotopic tracer methods for slow reactions and more usefully by NMR methods (Hunt, 1971; Stengle & Langford, 1967), using ^1H and ^{17}O , for fast reactions.

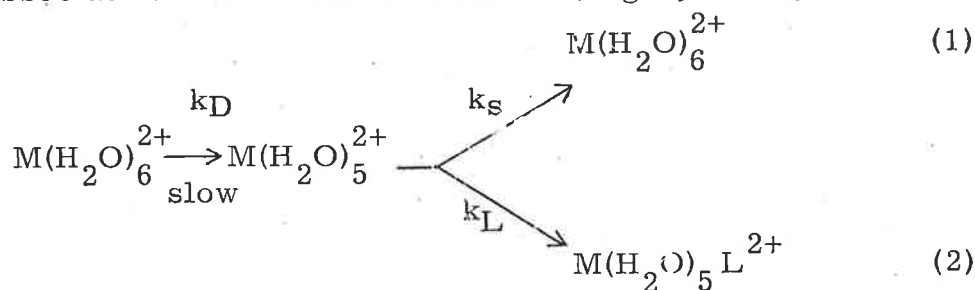
The exchange rates are generally quoted in terms of τ , the mean lifetime of one solvent molecule on the metal ion and for an n coordinate species.

$$\begin{aligned} \frac{d \text{ Exchange}}{dt} &= \frac{n}{\tau} \cdot [M(H_2O)_6^{2+}] \\ &= n \cdot k_{ex} [M(H_2O)_6^{2+}] \end{aligned}$$

Discussion of the variation in solvent exchange rate with metal ion (Swift & Connick, 1962), solvent (Benetto & Caldin, 1971) and coordinated ligands (Hunt, 1971) is unnecessary for a simple picture of the relation between substitution rates and solvent exchange rates, and will not be considered.

11.1.2 Substitution of a neutral ligand

In the absence of electrostatic forces between cation and ligand, the distribution of free ligand in a dilute solution of metal complex can be approximated by a Boltzman distribution. If a dissociative mechanism is assumed (Eigen, 1961),



then for solvent exchange (path (1))

$$\frac{-d \text{ Exchange}}{dt} = k_D [M(H_2O)_6^{2+}] = 6 k_{ex} [M(H_2O)_6^{2+}]$$

and for substitution of L (path (2))

$$\frac{d [M(H_2O)_5 L^{2+}]}{dt} = k_D [M(H_2O)_6^{2+}] \cdot \frac{k_L [L]}{k_S [H_2O]}$$

If $M(H_2O)_5^{2+}$, the five coordinate intermediate, shows no specificity in its reactions, then $k_L = k_S$.

$$\text{and } \frac{d[M(H_2O)_5 L^{2+}]}{dt} = k_D [M(H_2O)_6^{2+}] \frac{[L]}{[H_2O]}$$

$$= \frac{6 k_{ex}}{S} [M(H_2O)_6^{2+}] [L]$$

The observed second order substitution rate constant is related to the first order solvent exchange rate constant by

$$k_{sub} = \frac{6 \cdot k_{ex}}{[H_2O]} = 0.108 \text{ for water}$$

(see for example Benetto & Caldin, 1971 a, b; Shu & Rorabacher, 1972)

11.1.3 Substitution of an anionic ligand

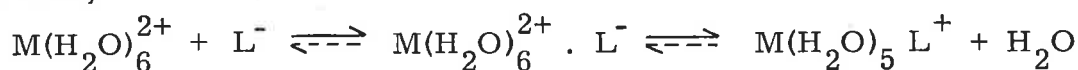
A solution containing cationic metal complexes and anionic free ligands does not show the Boltzman distribution observed for neutral ligands, due to electrostatic attractions. The cations tend to associate with anions to form "outer-sphere" complexes or ion-pairs. To relate the substitution rate to the solvent exchange rate in a simple manner, the Eigen (1961) substitution mechanism can be adopted. One must assume

- (a) a dissociative mechanism operates
- (b) association to form ion pairs does not affect the rate of the dissociative step
- (c) ligand and solvent show equal affinity for the five coordinated intermediate

For substitution from a contact ion pair (i. e. one in which cation and incoming anionic ligand are separated only by the solvent in the first coordination sphere of the metal ion), the argument is straight forward.

There are six solvent molecules in the coordination sphere of the metal ion. Seven of the eight octahedral faces are occupied by solvent and one by ligand. If dissociation of one of the solvents in the first coordination sphere occurs then assumption (c) implies a 1 in 8 chance of substitution taking place (i. e. of the ligand molecule occupying the vacated site)

We have;



$$\begin{aligned} \frac{d[M(H_2O)_5 L^+]}{dt} &= k_D' [M(H_2O)_6^{2+} \cdot L^-] \\ &= k_D' \cdot K_{IP} \cdot [M(H_2O)_6^{2+}] [L^-] \end{aligned}$$

but statistically $k_D' = \frac{k_D}{8} = \frac{6 k_{ex}}{8}$

$$\therefore \frac{d[M(H_2O)_5 L^+]}{dt} = \frac{6}{8} K_{IP} \cdot k_{ex} \cdot [M(H_2O)_6^{2+}] [L^-]$$

The observed second order rate constant for substitution of an anionic ligand is related to the first order solvent exchange rate constant by,

$$k_{sub} = \frac{6}{8} K_{IP} k_{ex}$$

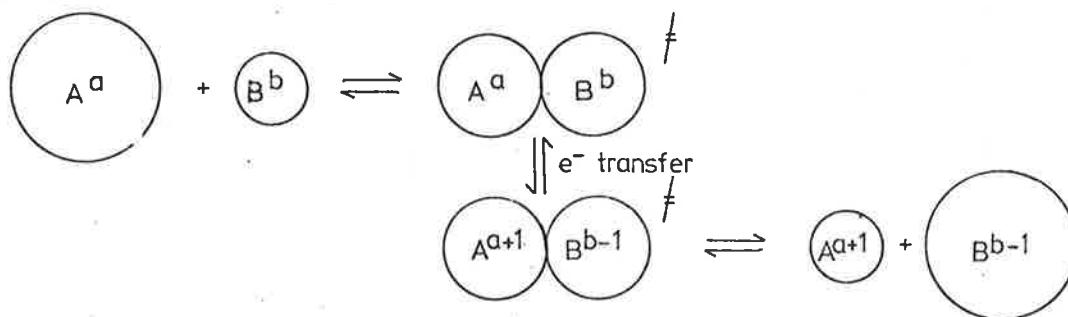
For the particular case of a divalent metal ion and a single-negatively charged ligand in water, K_{IP} is of the order of 1, hence $k_{sub} \approx k_{ex}$.

11.2 REDOX REACTIONS - OUTER SPHERE REACTION BETWEEN 2 METAL COMPLEXES

With few exceptions, redox reactions of transition metal complexes can be conveniently classified into inner and outer sphere mechanisms depending upon the nature of the transition state associated with electron transfer. The idealized cases of outer and inner sphere reactions will be discussed in 11.2 and 11.3. Some examples of reactions which cannot readily be classified are given in 11.5.

If, in the transition state associated with electron transfer, the first coordination spheres of both reactants retain the same ligands as

those present initially (though geometrically distorted), the mechanism is termed "outer-sphere". The reaction is visualized as occurring between flexible but discrete spheres representing reactants, which touch but do not interpenetrate in the transition state.



It is likely but not inevitable that reactions and products will differ in geometry due to the change in oxidation state. If this is the case some reorganization must accompany reaction, either preceding or following the instantaneous electron transfer expected from the Franck Condon principle.

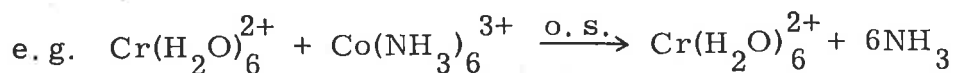
For electron transfer to take place some interaction of electronic wavefunctions of reactants and products must occur in the transition state. The lack of interpenetration in the outer sphere transition state suggests that the interaction is small. Marcus (1956, 1963, 1968) has used this assumption to derive a theoretical treatment of the rates of outer sphere electron transfer reactions (For further discussion see 11.2.2 and 13.9).

11.2.1 Qualitative observations

From the definition of the outer sphere reaction certain qualitative observations can be predicted. Experimentally these observations have been used to assign mechanisms to various reactions.

(a) Products

If one (or both) of the initial products of the electron transfer is sufficiently stable for observation then the occurrence of an outer sphere mechanism can be inferred if the coordination sphere(s) has been retained in the corresponding product.



The first coordination sphere of the chromium remains intact (Zwicker & Taube, 1961)*

(b) Intermediates

Interactions between reactants in the transition state of an outer-sphere reaction are, by definition, weak. It is probable that at all other times in the reaction the interactions are similarly weak and consequently it is unlikely that an intermediate of structure related to the transition state will be observed (cf 11.3.1)

11.2.2 Quantitative observations

From the assumption of negligible interaction in the transition state it is expected (Marcus, 1963) that for reaction of a given reductant (or oxidant) with a series of related complexes a plot of the free energy of activation, $\Delta G^\ddagger$, against the overall free energy change, ΔG° , should be linear with a slope of 0.5 if the reaction mechanisms are outer sphere. In practice this relation holds only approximately and the proportionality constant of 0.5 is observed only when the overall free energy changes are small (For examples see Rillema & Endicott, 1972; Hyde, Davies & Sykes, 1972). A more detailed discussion of the effect of ΔG° on the rates of reactions of halogen radical anions is given in 13.9

* Footnote

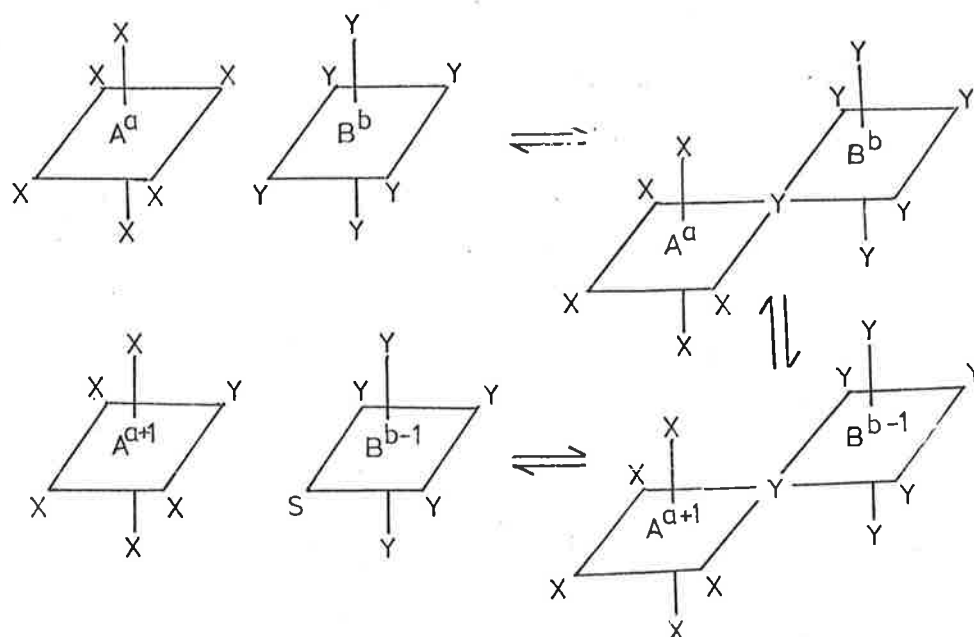
The timescale of the redox reaction determines the minimum timescale in which an initial product can be observed and consequently the stability necessary for product identification.

e.g. If the redox reaction has a half life or 1 μs then a product which is stable for longer than 1 μs may be observable; but if the half time for the redox reaction is 10^3 s then the product must be stable for at least 10^3 s. Development of very fast (10^{-9} - 10^{-12} s) reaction systems may, with suitable choice of reactions, provide more information on the initial products.

11.3 REDOX REACTIONS - INNER SPHERE REACTION BETWEEN 2 METAL COMPLEXES

The inner-sphere mechanism requires a definite change in the ligands of the first coordination sphere of one of the reactants because as Taube (1970) has said "electron transfer takes place within a single primary bond system". The change, visualized as substitution of one reactant into the coordination sphere of the other, requires expulsion of at least one ligand (often solvent) from the substituted reactant. In the transition state for electron transfer there is considerable overlap of electronic wave functions.

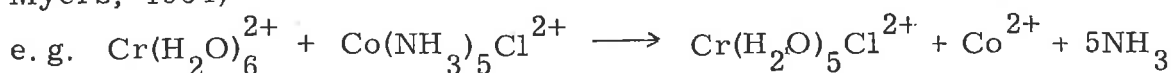
The weak interaction model proposed for the outer-sphere reactions is quite inappropriate for inner-sphere reactions. The mechanism approaches that of a substitution reaction to form a dinuclear intermediate or transition state with one or more bridging ligands followed by an intramolecular electron transfer.



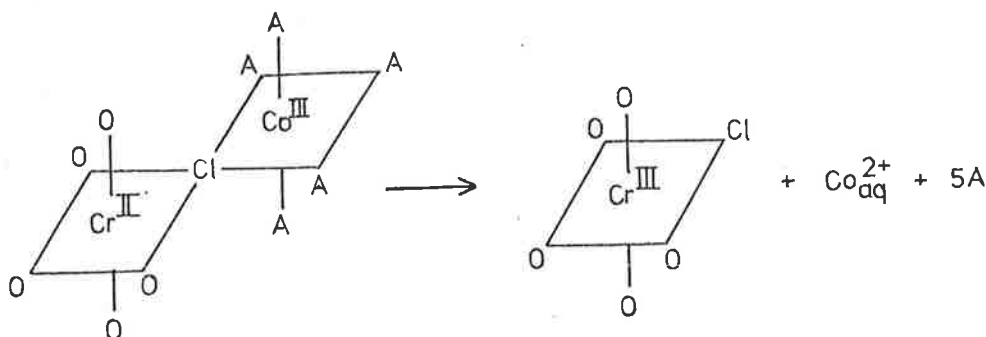
11.3.1 Qualitative observations

(a) Products

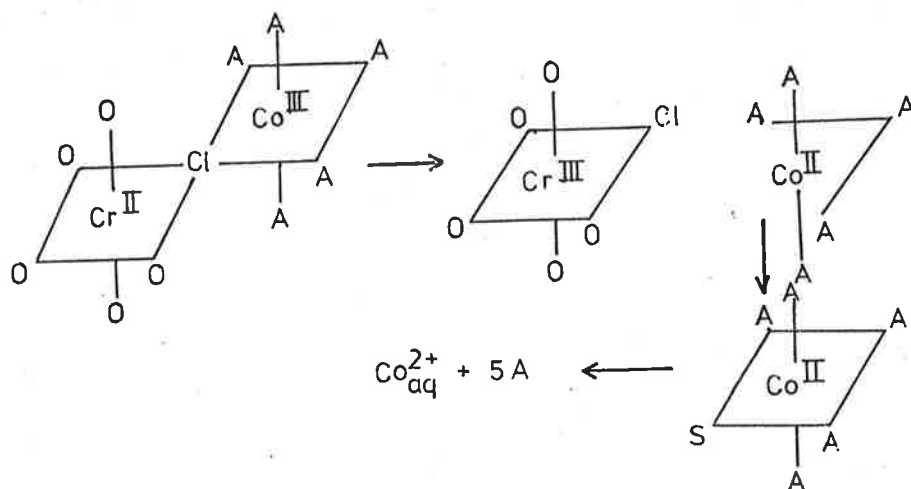
The Franck-Condon principle requires that the position of the shared ligand(s) is the same immediately before, during, and immediately after electron transfer. The final fate of the shared ligand(s) depends upon the processes occurring after electron transfer and is irrespective of the reactant to which the ligands originally belonged. In most cases, particularly those involving first row transition metal ions, the higher oxidation state complex is more resistant to substitution than the lower one. As a result the oxidant generally contributes the shared ligand and the oxidised product is usually the only one that is sufficiently stable to observe on the time scale of the experiment. In such instances the shared ligand is invariably transferred as a result of electron transfer (e.g. Taube & Myers, 1954)



This may be a consequence of the concerted breakdown of the bridged complex and the unstable fragment,



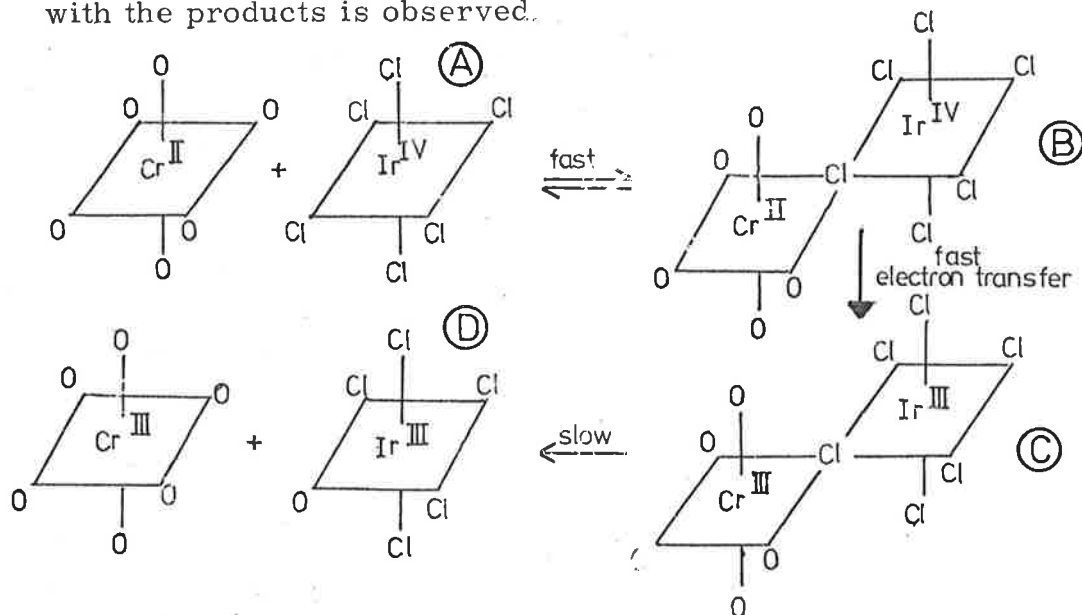
or simply the greater affinity of the stable complex for the ligand.



Observation of ligand transfer in the initial products of the electron transfer is unequivocal proof of an inner-sphere mechanism.

(b) Intermediates

The extent of interaction in the transition state of an inner-sphere reaction is often sufficiently large for a dinuclear intermediate of structure related to the transition state to exhibit a finite existence. The oxidation states in the intermediate may correspond to reactants or products. A good example of this can be seen in the reaction of chromium (II) with hexachloroiridate (IV), (Sykes & Thorneley, 1970) where a bridged intermediate (C) which exhibits properties associated with the products is observed.



The observation of any inner-sphere intermediate complex

during the course of the reaction is conclusive proof that an inner-sphere mechanism is operative. (e. g. Patel, Ball, Endicott & Hughes, 1970).

11.3.2 Quantitative observations

In situations where qualitative observations are not possible or do not unequivocally define the mechanism correlations between the rates of inner-sphere reactions and other parameters of the system may be of use in suggesting the type of mechanism. Mechanistic assignments based on quantitative observations are seldom conclusive.

(a) Relation to substitution rates

The inner-sphere mechanism involves substitution of one reactant into the coordination sphere of the other and so no matter how fast the subsequent electron transfer process is the upper limit to the rate of the overall reaction is imposed by the rate of substitution. If the substitution is faster than the electron transfer, the mechanism may be more precisely labelled "inner-sphere substitution controlled". Section 11.1 relates the substitution rates to solvent exchange rates. Examples of substitution controlled inner-sphere reactions are given in 13.1 and 13.2.

Not all inner-sphere reactions are substitution controlled. In many cases the electron transfer step is considerably slower than the substitution and the mechanism can be described as "inner-sphere electron transfer controlled". The overall rate constant for such a reaction must be less than the substitution rate.

(b) Free energy relationships

The rate of substitution in a metal complex bears no relation to the free energy change of any redox reaction, consequently no correlation between free energy change and the rate of a substitution controlled inner-sphere reaction would be expected. On the other hand, inner-sphere electron transfer controlled reactions might be expected to show some dependence of $\Delta G^\ddagger$ on ΔG^0 , although direct application

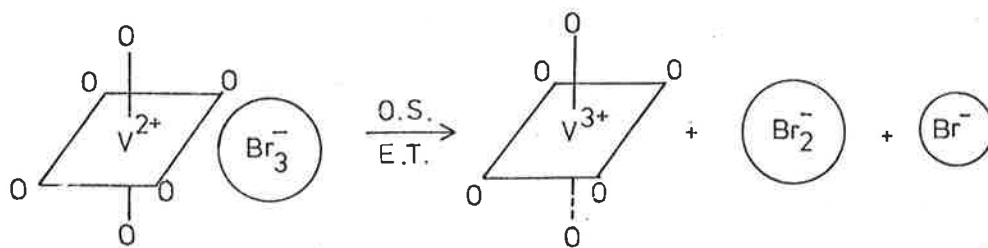
of the Marcus theory to this situation, where the "slight interaction" model is clearly inapplicable, would be a gross simplification. Some success in applying the Marcus relationship to inner-sphere reactions has been achieved (Haim & Sutin, 1966; Fay & Sutin, 1970) but the applicability is less general and less precise than for outer sphere reactions.

11.4 REDOX REACTION BETWEEN A METAL COMPLEX AND A SIMPLE ANION OR NEUTRAL MOLECULE

The concept of inner and outer sphere reactions developed for reaction between metal complexes can be applied equally well to reaction between a metal complex and a simple neutral or anionic redox agent. The terms inner and outer-sphere refer to the coordination sphere of the metal complex. The anions are considered to possess no discrete or lasting coordination sphere (Subramanian & Fisher, 1972; Stengle, Pan & Langford, 1972).

11.4.1 Outer sphere reactions

The reaction will be "outer-sphere" if the first coordination sphere of the metal complex remains intact in the transition state associated with electron transfer. Electron transfer must take place through or between ligands in the coordination sphere of the metal ion.



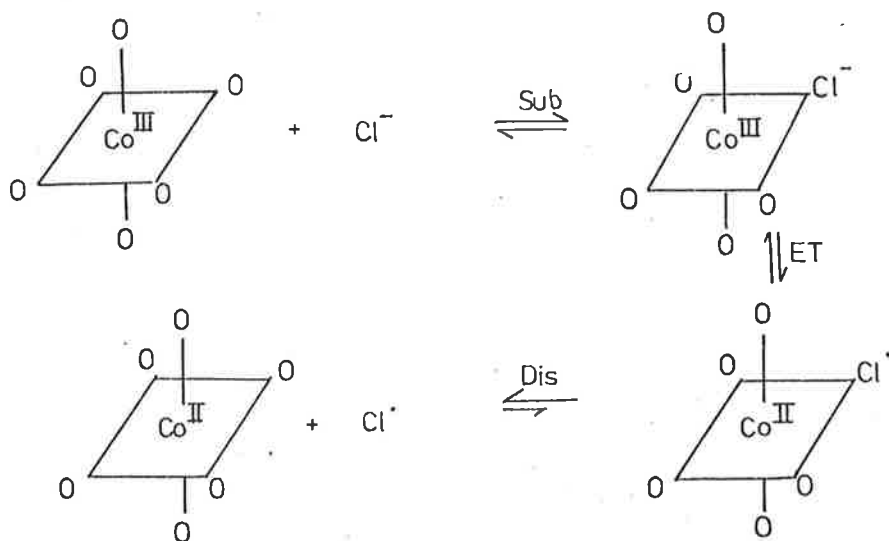
This mechanism requires that the initial metal ion product retains its original coordination sphere.

The degree of interaction between a cationic metal complex and

an anion is expected, on purely electrostatic grounds, to be greater than between two metal complexes of the same charge type. The observation of ion pair formation between inert complexes and free anions is direct evidence of this interaction. Consequently the Marcus model of slight interaction is probably inappropriate even for outer sphere reactions of this kind. Deviations from the expected linear free energy relationships may be expected (see 11.2.2).

11.4.2 Inner sphere reactions

If the metal complex is rapidly substituted (labile) then substitution of the anion or neutral molecule into its first coordination sphere followed by electron transfer through a primary bond system, may be preferred over outer sphere electron transfer. This mechanism is inner-sphere in type and in contrast to the outer sphere case it can be seen that the first coordination sphere of the metal ion in the transition state for electron transfer has already been penetrated by the ligand involved in the electron transfer.



In cases where the overall rate of reaction is limited by the rate of the electron transfer step an intermediate complex of the two reactants may be observed (e. g. CoCl^{2+} in the oxidation of chloride by cobalt (III) aquo ions; Conocchioli, Nancollas & Sutin, 1965). For

this type of "electron transfer controlled inner-sphere reaction" the rate of the redox reaction will be less than the rate of substitution on the metal complex (see 11.1.2, 11.1.3).

Where the electron transfer step is rapid compared to the substitution step the reaction is limited by the rate of substitution which should be related to the rate of solvent exchange on aquo metal cations (see 11.1.1).

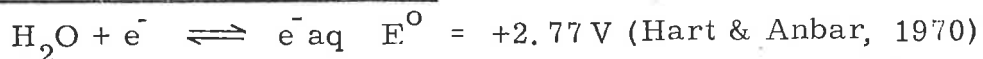
In both cases, observation of the initial product or an intermediate can conclusively characterise the mechanism. If the initial metal ion product contains the oxidised or reduced anion (or neutral molecule) then it is clear that reaction has proceeded by an inner-sphere mechanism.

11.5 REDOX REACTION BETWEEN A METAL COMPLEX AND A RADICAL

With few exceptions (see 11.5.4, 11.5.5, and 11.6) the study of metal complex - radical[†] reactions has been restricted to organic radicals (Collinson, Dainton, Mile, Tazuke & Smith, 1963; Denisov, 1971) or the primary radiation - chemically produced radicals, e^-_{aq} , H , OH (Anbar & Neta, 1967).

The investigators have generally been content to evaluate a rate constant, very few activation energies have been determined, and still fewer mechanistic observations have been made.

11.5.1 Aquated electrons, e^-_{aq}



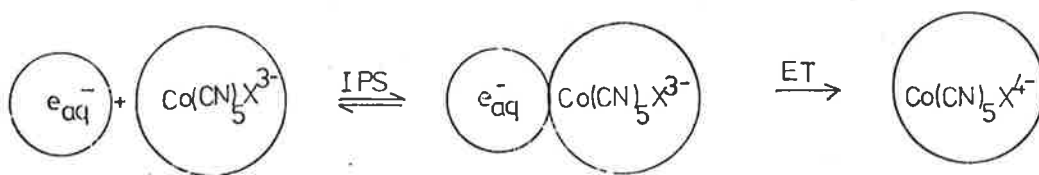
When its redox behaviour is compared with that of other anions (for example halide ions, see 11.4), the simplest of all radical species, e^-_{aq} , is perhaps anomalous.

[†] Footnote

"Radical" refers to a species with an unpaired "p" or "s" electron and excludes such species as ferric ion which have unpaired "d" electrons.

Unlike other anions it appears to possess a distinct but labile coordination sphere, similar but oppositely oriented to the coordination sphere around labile metal aquo ions. Current models (see Hart & Anbar, 1970) for the aquated electron suggest a tetrahedral arrangement of water molecules around a small negative centre.

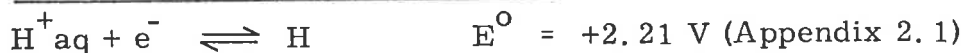
The rate constants for reaction of e^-_{aq} with metal complexes, with the possible exception of Cr^{2+}_{aq} (Anbar & Hart, 1965), are in excess of the possible substitution rate on the complexes and the metal must retain its coordination sphere on approach to the transition state. In a study of the rates of reaction of e^-_{aq} with a series of cobalt (III) complexes, $Co(CN)_5X^{3-}$, Venerable (1971) established a correlation between the rate constant and the ligand field splitting parameter of the heteroligand, X^- . Similar trends have been observed in the reduction of Co (III) complexes by the outer sphere reductants V^{2+}_{aq} and $Cr(bipy)_3^{2+}$ (Candlin, Halpern & Trimm, 1964). The probable inner sphere reductants Cr^{2+}_{aq} and Eu^{2+}_{aq} (Candlin et al., 1964) and U^{3+}_{aq} (Wang & Espenson, 1971) show erratic but often opposite trends. Venerable (1971) has interpreted his results as showing that aquated electrons react with inert cobalt (III) complexes by an outer sphere mechanism of the type expected in the reaction of two metal complexes, i. e. the electron transfer takes place between distinct coordination spheres and through two ligands.



It is clear that retention of the e^- aq coordination sphere cannot be demonstrated by product analysis.

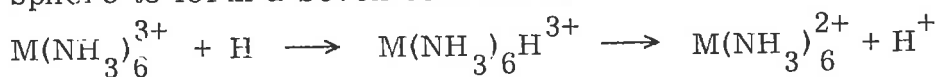
11.5.2 Hydrogen atoms, H.

(a) Reduction by hydrogen atoms



Hydrogen atoms cannot be observed spectrophotometrically in aqueous solution, and kinetic spectrophotometry is possible only if the other reactant or a product has an accessible absorbance. The great majority of hydrogen atom rate constants have therefore been determined by competition methods (Anbar & Neta, 1967).

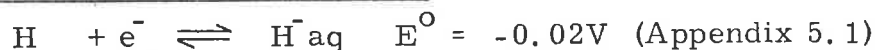
The rate constants for reaction with transition metal complexes are in excess of the substitution rates on the metal complexes with the exception of the reactions with Cu^{2+}_{aq} and Mn^{2+}_{aq} for which the rates are very close to the expected substitution rates. This suggests that (possibly excepting Cu^{2+}_{aq} and Mn^{2+}_{aq}) reactions of hydrogen atoms with metal complexes proceed by an outer sphere mechanism (see 11.4.1). In a study of the reduction of hexaammine complexes of Co (III) and Ru (III) by hydrogen atoms and hyper-reduced metal ions, Navon & Meyerstein (1970) proposed that hydrogen atoms reacted by an inner sphere mechanism in which they penetrated the first coordination sphere to form a seven coordinate intermediate.



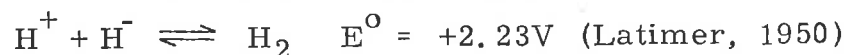
This mechanism was proposed because the relative rate constants of the two hexaammines and $Co(NH_3)_5H_2O^{3+}$ with hydrogen atoms were not in the order observed for other reductants, known to react by an outer sphere mechanism. A more recent study of the reactions of aliphatic radicals with Co (III) and Ru (III) hexaammines (see 11.5.6) by Cohen & Meyerstein (1972) has shown that these reactions follow the same trends as the hydrogen atom reactions. The aliphatic radicals are too large to penetrate the first coordination sphere of the metal

complex. The special features of these reactions are unresolved.

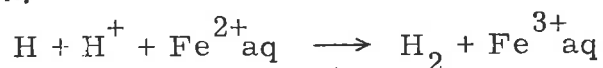
(b) Oxidation by hydrogen atoms



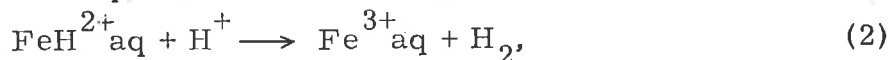
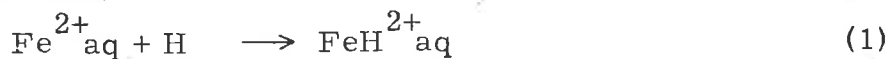
In basic solution hydrogen atoms are weak oxidising agents, but in acid solution the subsequent reaction of hydride ions with hydronium ions provides a larger ΔG^0 .



The oxidation of ferrous ion by hydrogen atoms (Czapski & Stein, 1959; Jayson, Keene, Stirling & Swallow, 1969) appears to be the only well documented oxidation of a metal ion by hydrogen atoms. Extensive work on the radiolysis of ferrous solutions has shown that hydrogen atoms are quantitatively converted to ferric ions in acid solution.



Jayson et al. (1969) found that in the pulse radiolysis of de-aerated ferrous solution an intermediate was formed, which disappeared by reaction with hydronium ions, and was assumed to be a complex of ferric ions and hydride ions, displaying an optical absorption at 325 nm with $\epsilon \sim 500$.



This "hydride" mechanism had previously been proposed by Halpern, Czapski, Jortner & Stein (1960) and Czapski, Jortner & Stein (1961).

≠ Footnote

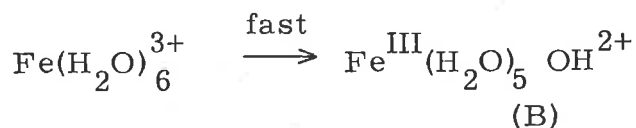
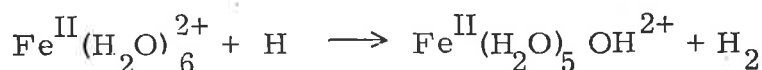
Assuming the intermediate is $\text{FeH}^{2+} \text{aq}$ the expected position of the LMCT band can be calculated as 990 nm, by comparison with the ferric halide complexes. Errors involved in the estimate could not account for the discrepancy. It is apparant that either the complex is not $\text{FeH}^{2+} \text{aq}$ or that the absorption band is not due to LMCT (see 1.4.2)

Consideration of the thermodynamics of the above mechanism using the estimates of E^0 values given in Appendix 2.1 casts some doubt on its validity. If the ferric hydride complex is not more than a few kJ/mol more stable than free ferric and hydride ions then step (1) is unfavourable by about 75 kJ/mol, corresponding to an equilibrium constant for step (1) of about $10^{-12} \text{ l mol}^{-1}$. This value implies that the $\text{FeH}^{2+}_{\text{aq}}$ complex would not be present in sufficient concentration to observe in the pulse radiolysis experiments, and that the reverse rate constant, k_{-1} , would have to have the impossibly high value of about 10^{19} s^{-1} . Either the mechanism proposed is incorrect or the $\text{FeH}^{2+}_{\text{aq}}$ complex is considerably ($\sim 80 \text{ kJ/mol}$) more stable than free ferric and hydride ions; comparison with halide and pseudo halide complexes of ferric ions suggests that this degree of stability would be unprecedented.

Mechanisms involving H_2^+ as the oxidant,



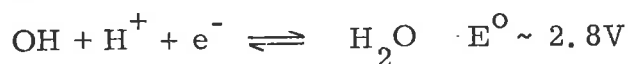
can be eliminated on kinetic grounds because it has been shown that the rate of formation of H_2^+ from H is less than $10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ (Matheson, 1964); 10^4 times slower than the oxidation of ferrous by hydrogen atoms. This and a hydrogen atom abstraction mechanism can also be eliminated because a relatively long lived intermediate is observed. (A)



Neither intermediate A or B could be expected to show the milli-second lifetimes observed by Jayson, Keene, Stirling & Swallow, (1969). On the available information, description of the mechanism is not possible. It is apparent that overall the reaction involves oxidation of the ferrous ion but none of the proposed mechanisms fit

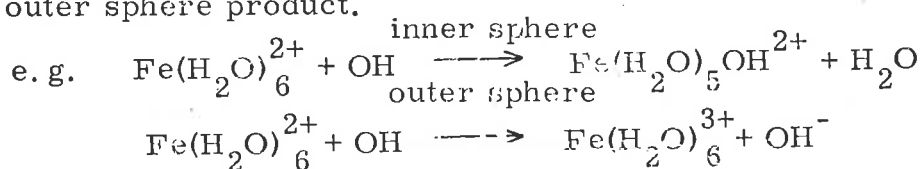
the experimental facts. Considerable experimental skill will be needed to devise experiments which will finally establish the intimate mechanism of this important reaction.

11.5.3 Hydroxyl radicals OH



Hydroxyl radicals are powerful oxidising agents, in both acid and alkaline solution, capable of oxidising many transition metal complexes. The rates of reaction of Cr^{2+}aq , Cu^{2+}aq , and Mn^{2+}aq with hydroxyl radicals are about the same as the substitution rate on the metal cation. In all other documented cases (Anbar & Neta, 1967) the rates are significantly greater than the substitution rates and an inner-sphere mechanism cannot be operating. With the exception of Cu^{2+}aq all other aquo metal ions show a small but positive correlation between $\Delta G^\ddagger$ and ΔG° for the reaction (see Fig. 11.5A). The slope of the linear free energy plot is 0.075, much smaller than the expected 0.5 for a transition state of negligible interaction (Marcus, 1963). If an outer-sphere mechanism operates in these cases it is clear that the effect of ΔG° is substantially reduced.

Product analysis is of little help in elucidating mechanisms of hydroxyl radical reactions in aqueous solution. Oxidation of ferrocyanide proceeds at a diffusion controlled rate to produce ferricyanide. In this case the reaction proceeds by an outer-sphere mechanism and ferrocyanide does not fit the linear free energy plot derived for the aquo complexes. Product observations for aquo/hydroxo complexes must be performed very rapidly as fast protonation reactions are capable of converting the inner-sphere product to the outer sphere product.



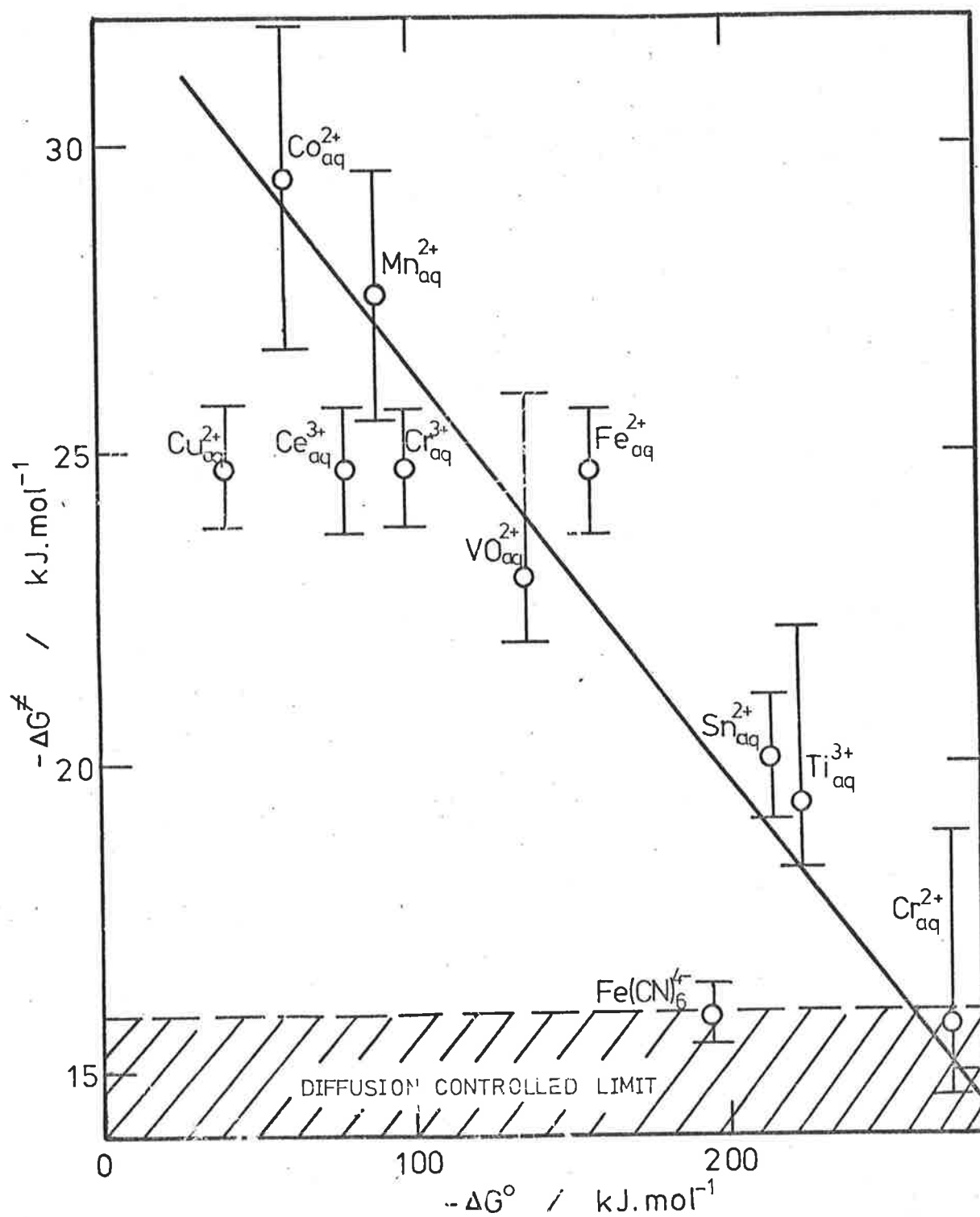
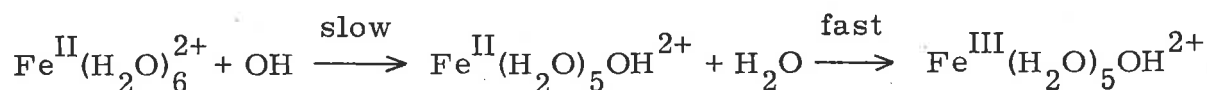


Fig. 11.5A Linear Free Energy Plot - $\text{M}^{n+}_{\text{aq}} + \text{OH}^-$

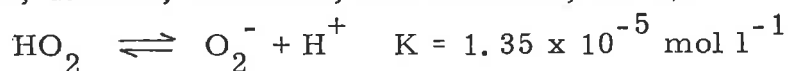
This reaction has been examined by Swallow (1966), who claims that the initial product is $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, ruling out an inner-sphere or hydrogen atom abstraction mechanism.



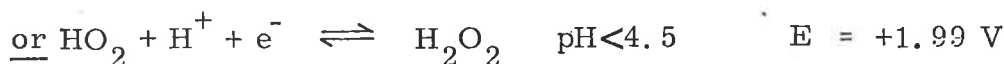
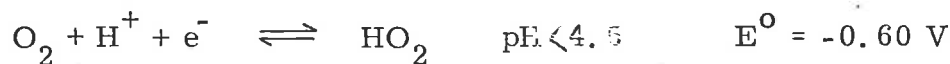
If Swallow's observation is correct and one assumes that Fe^{2+} is not exceptional then the other aquo metal ions (with the exception of Cu^{2+} which does not fit the free energy relationship) presumably also react by an outer-sphere mechanism. The departure from the classical linear free energy relationship must be due to the inapplicability of the simple Marcus treatment.

11.5.4 Peroxy radicals, HO_2 , O_2^-

Hydroperoxy radicals have a pK_a of 4.88 ± 0.10 (Behar, Czapski, Rabani, Dorfman, and Schwarz, 1970).



Both O_2^- and HO_2 can act as oxidizers or reducers (Appendix 2.2).



The rates of peroxy radical reactions have been the subject of much conjecture because peroxy radicals are intermediates in the oxidation of hydrogen peroxide and reduction of oxygen. Barb, Baxendale, George & Hargrave (1951) obtained rate constant ratios for reactions of HO_2 with Fe^{2+}aq , Fe^{3+}aq , and Cu^{2+}aq from the catalyzed decomposition of hydrogen peroxide. Absolute rate constants (see Table 11.5A) have been calculated using the most recent estimate of the rate constant for the Fe^{2+} , HO_2 reaction (Jayson, Parsons & Swallow

1973). The work of Berdnikov, Kozlov & Purmal (1969) appears to be in conflict with the early work of Barb et al (1951)

Table 11.5A

Rates of HO_2 reactions with metal ions

M^{n+}	Reaction	Rate constant $1 \text{ mol}^{-1} \text{ s}^{-1}$	Year	Reference*
Fe^{2+}	Oxidation	$(1.2 \pm 0.05) \times 10^6$	1973	a
Fe^{2+}	Oxidation	7.3×10^5	1964	b
Fe^{3+}	Reduction	8×10^4	1951	c
Cu^+	Oxidation	4.3×10^9	1969	d
Cu^{2+}	Reduction	1.5×10^7	1962	e
Cu^{2+}	Reduction	5×10^6	1951	c
Cu^{2+}	Reduction	1.1×10^8	1969	d

*References

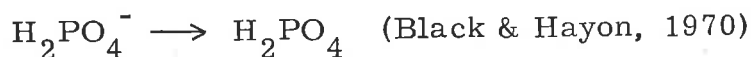
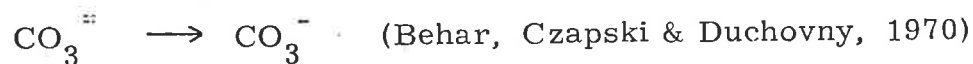
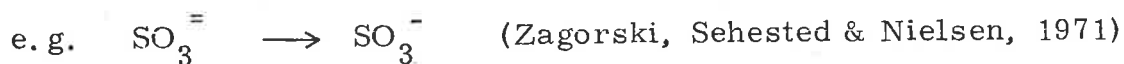
- (a) Jayson, Parsons and Swallow (1973)
- (b) Keene (1964)
- (c) Barb, Baxendale, George and Hargrave (1951)
- (d) Berdnikov, Kozlav and Purmal (1969)
- (e) Baxendale (1962)

The rate of reaction of ferric ions with HO_2 is at least 10^3 times faster than substitution on hexaaquoferrous ions (see Hewkin & Prince, 1969), and the mechanism for this reaction must be outer sphere. The other reactions could proceed by an inner sphere mechanism but in the case of ferrous ions an intermediate, thought to be an outer-sphere complex of $\text{Fe}^{3+} \text{aq}$ and HO_2^- is observed

(Jayson, Parsons & Swallow, 1973). If their interpretation of the nature of the intermediate is correct the reaction must proceed by an outer sphere mechanism. No other mechanistic evidence is available on these reactions. Unfortunately assignment of mechanism for peroxy radical reactions is impeded by a lack of knowledge of the spectra and properties of the expected products (e. g. $\text{Fe}(\text{HO}_2)^{2+}$, $\text{Fe}^{3+} \cdot \text{HO}_2^-$, etc.)

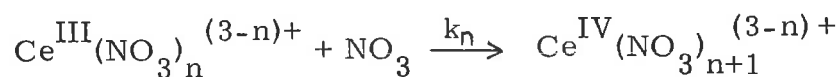
11.5.5 Oxy radicals and oxyradical anions

Flash photolysis and pulse radiolysis of oxyanions produces transients generally attributed to the corresponding oxyradicals.



etc.

Very few reactions of these radicals, apart from disproportionation, rearrangement or reaction with solvent have been studied. The only reported reaction with a metal complex is the reaction of Ce(III) nitrate complexes with nitrate radicals ($\text{NO}_3^{\cdot}$) produced by flash photolysis of ceric nitrate complexes. The observed rate constants, k_n , for the reactions,



were found to be in the order $k_5 \ll k_1 < k_2 < k_3 < k_4$, with activation energies of 4 - 8 kJ mol⁻¹ for k_{1-4} but >24 kJ mol⁻¹ for k_5 . Despite the low activation energies the rate constants k_{1-4} are only of the order of 10⁶ mol⁻¹ s⁻¹. It is assumed that these reactions are diffusion controlled with a sterically difficult transition state, possibly involving bidentate coordination. k_5 is considerably slower than the other

rate constants because of its higher activation energy, which is assumed to reflect the difficulty of forming a seven coordinate transition state. (Glass & Martin, 1970; Martin & Glass, 1970).

11.5.6 Small organic radicals

Organic compounds such as alcohols, amines, acids and carbonyl compounds are frequently employed to scavenge hydroxyl radicals in radiation chemistry experiments (Anbar & Neta, 1967). Aliphatic radicals are formed but little is known of their chemistry. Cohen and Meyerstein (1972) have studied the reactions of some of these radicals with cobalt (III) and ruthenium (III) hexaammines and Cu^{2+} aq ions. Product observation in the reaction of methoxy radicals with $\text{Ru}(\text{NH}_3)_6^{3+}$ shows that the mechanism is as expected, outer sphere ($k = 4.1 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$)



Formation of formaldehyde rather than methanol implies that the reaction does not proceed by hydrogen atom abstraction but rather by simple outer sphere electron transfer. Product analysis was not performed on the other systems studied.

The mechanisms of the Cu^{2+} aq reactions were not investigated but for the three radicals studied, CH_2OH , CH_3CHOH and $(\text{CH}_3)_2\text{COH}$ the rate constants fall in the range 4.5×10^7 to $1.1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$, slightly slower than the reactions with hydrogen atoms ($k \sim 5 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$; Anbar & Neta, 1967), and hydroxyl radicals ($k = 3.5 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$; Baxendale, Fielden & Keene, 1965), and about the same rate as the most recent estimate of the rate of reaction with HO_2 ($k = 1.1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$; Berdnikov, Kozlav and Purmal, 1969). The approximate constancy of the rate constant with change in oxidant (or reductant) suggests that the reactions may be inner sphere, possibly controlled by the rate of substitution on Cu^{2+} aq. Estimates of the substitution rate for Cu^{2+} aq vary but the true value is probably

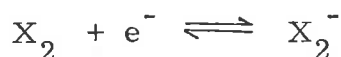
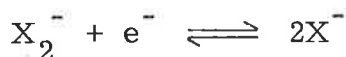
between 10^8 and $10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ (Hewkin & Prince, 1969), in reasonable accord with the rate constants quoted above.

11.5.7 Macro-organic radicals

The reactions of some macro-organic radicals and large peroxy organic radicals with metal complexes have been studied in relation to polymerizing systems. In almost all cases the reactions are certainly outer sphere and often involve considerable steric barriers to reaching the transition state. These reactions have recently been reviewed (Denisov, 1971).

11.6 REDOX REACTIONS BETWEEN METAL COMPLEXES AND HALOGEN RADICAL ANIONS

A review of the formation and some properties of halogen radical anions was given in Section 1. Halogen radical anions can act as both oxidising and reducing agents.



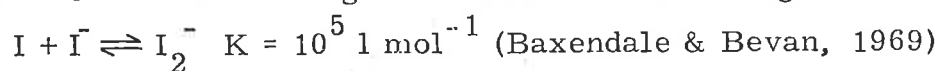
The redox potentials of these couples have been estimated to support proposed reaction schemes (Carter & Davidson, 1952; Haim & Taube, 1963; Welton and Higginson, 1965). Malone & Endicott (1972) estimated the E^0 values for the three half reactions using standard free energies of formation and estimating unknown ones. (A similar calculation for Br_2^- and I_2^- has recently been done by Woodruff & Margerum 1973). We have calculated (Appendix 2.3) a consistent set of values assuming that halogen radical anions are intermediates in the reduction of halogens to halide ions. The values which are quoted in Table 11.6 agree satisfactorily with previously published values.

Table 11.6

 E° Values

X	Year	References	$X + e^{-} \rightleftharpoons X^{-}$	$X_2 + e^{-} \rightleftharpoons 2X^{-}$	$X_2 + e^{-} \rightleftharpoons X_2^{-}$
Cl	1973	a	+2.59	+2.29	+0.43
	1972	b	+2.6	+2.3	+0.6
	1952	c	-	+2.3 - 2.5	-
Br	1973	a	+2.08	+1.77	+0.41
	1973	d	+2.06	+1.67	+0.51
	1972	b	+2.2	+1.9	+0.3
	1965	e	-	-	+0.54
	1952	c	+1.9	+1.69	+0.46
I	1973	a	+1.31	+1.00	+0.06
	1973	d	+1.42	+1.13	+0.11
	1972	b	+1.4	+1.1	+0.3
	1965	e	+1.3	+1.0*	+0.1*
	1963	f	+1.27	+1.04	-

Notes: * Calculated from given values for I assuming



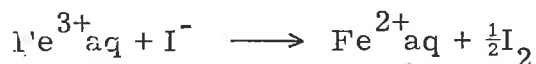
References:

- (a) Current estimate (Appendix 2.3)
- (b) Malone and Endicott (1972)
- (c) Carter and Davidson (1952)
- (d) Woodruff and Margerum (1973)
- (e) Welton and Higginson (1965)
- (f) Haim and Taube (1963)

Halogen radical anions are relatively powerful oxidising and reducing agents, Cl_2^- being the strongest oxidiser and weakest reducer and I_2^- the strongest reducer and weakest oxidiser. They are easily observed spectrophotometrically in $\mu\text{mol l}^{-1}$ concentrations, relatively easily generated, their substitution behaviour is typical of a simple anion and their products are well characterized. They provide a near ideal "probe" for investigating redox mechanisms, especially for metal complexes.[‡]

11.6.1 Halogen radical anions as proposed intermediates

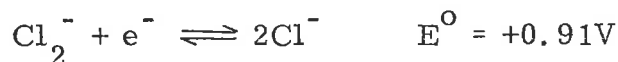
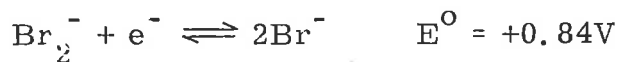
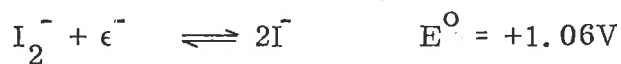
The first reactions of halogen radical anions with metal complexes were proposed by Wagner (1924) in the study of the reaction of ferric ions with iodide ions.



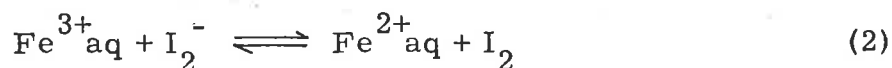
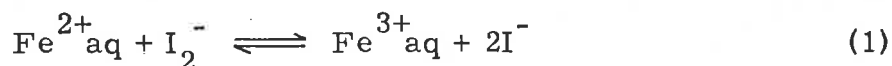
Wagner proposed that I_2^- formed in the rate determining step reacted with both ferrous and ferric ions.

[‡] Footnote:

Lilie (1972) has directly investigated electrode processes occurring in pulse irradiated halide solutions by polarography. He claims to have measured the following E° values.



The values are internally inconsistent; the E° for Cl_2^- must be higher than Br_2^- which in turn must be higher than I_2^- . With the exception of I_2^- the values show no relation to thermodynamically estimated values which are consistent with available experimental data. The large discrepancy is almost certainly due to the effect of irradiation on the dropping mercury electrode used for polarographic determination. (cf Airey, 1973)

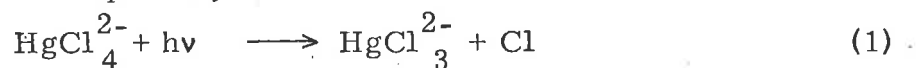


Fudge and Sykes (1952) made the first quantitative observation when they used the same scheme to derive a rate constant ratio k_1/k_2 of 7.

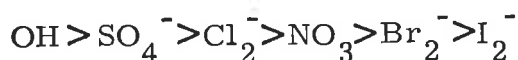
In the period between 1924 and the first direct observation of halogen radical anions by Grossweiner & Matheson in 1955, several other reaction schemes including halogen radical anions were proposed. The majority of these involved photochemical initiation. (e.g. Allmand & Young, 1931; Callow, Griffith & McKeown, 1939; Rutenberg & Taube, 1950; King & Pandow, 1953). Since 1955 a large number of redox reaction schemes involving halogen radical anions have been proposed both in oxidation of halide ions by metal ions (e.g. Co (III), Mn (III)) and reduction of halogens by metal ions (e.g. V (II), U (IV)). These reaction schemes will be covered in more detail in section 13 where they are directly relevant to the reactions being discussed.

11.6.2 Directly observed reactions of halogen radical anions - Rates

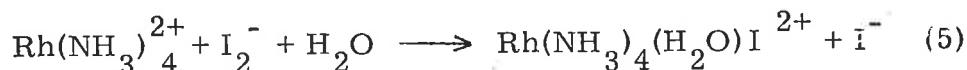
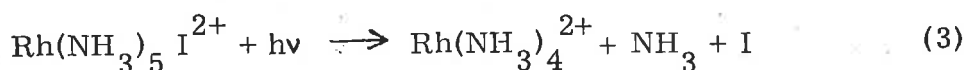
Radical reactions of halogen radical anions have been discussed in Part 1 of this thesis. The first redox reactions of X_2^- with an added substrate to be directly studied were reported by Langmuir and Hayon (1967). They found that Cl_2^- produced from mercuric chloride complexes,



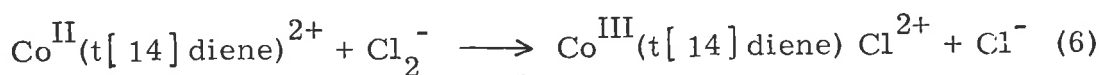
reacted with hydrogen peroxide, oxalate and short chain aliphatic alcohols with rate constants around $10^8 \text{ l mol}^{-1} \text{ s}^{-1}$. Br_2^- reacted more slowly ($k \sim 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$) with the same substrates. No reaction of I_2^- with the alcohols could be detected ($k < 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$). These rate constants were used as a measure of the oxidising power of the various radical species. Comparison with other radicals suggested that the order of oxidising power was:



The first report of a directly observed reaction between a metal complex and halogen radical anions was by Kelly & Endicott (1970) in the study of the charge transfer photochemistry of iodopentaamminerhodium (III) ions. They found that when Rh(II) was produced as a flash photolysis product the half life of I_2^- was only 70% of that in a system which did not produce Rh(II).



Kelly & Endicott (1972) estimated that the rate constant k_5 was $\approx 3 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. In a similar study on the photochemistry of various chloroamminecobalt (III) complexes (Caspari, Hughes, Endicott and Hoffman, 1970) it was found that although $\text{Co}^{2+}_{\text{aq}}$ was relatively unreactive to Cl_2^- (See 13.2), the reduced fragment from the photolysis of Co^{III} (trans [14] diene) Cl_2^+ reacted with an estimated rate constant of $\sim 1.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.



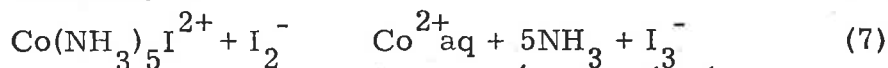
Malone & Endicott (1972) revised this estimate in a systematic survey of the oxidation of $\text{Co}^{\text{II}}(\text{t}[14] \text{ diene})^{2+}$ by X_2^- radical anions. The rate constants they obtained are listed in Table 11.6B.

Table 11.6B

$\text{Co}^{\text{II}}(\text{t}[14] \text{ diene})^{2+} + \text{X}_2^-$: Rate constants

Cl_2^-	$(1 \pm 0.4) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$
Br_2^-	$(1.45 \pm 0.1) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$
I_2^-	$(7.2 \pm 0.8) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$

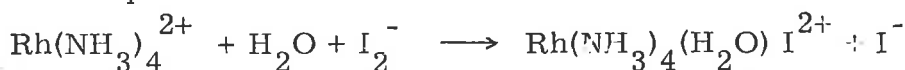
From an intensity dependence of the quantum yield for $\text{Co}^{2+}_{\text{aq}}$ formation from $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{I}^{2+}$ they also obtained indirect evidence for the reaction,



with a rate constant, k_7 , of $2.5 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

11.6.3 Directly observed reactions of halogen radical anions - Mechanisms.

The reaction of I_2^- with $\text{Rh}(\text{NH}_3)_4^{2+}$ produces $\text{Rh}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$ (Kelly & Endicott, 1972); from this product which is presumably the initial product (Rh(III) is substitution inert) it is clear that an inner sphere mechanism is operative. The incorporation of solvent water into the product



rather than the production of a di-iodo complex

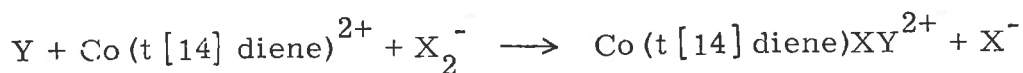


suggests that I_2^- is capable of occupying only one ligand site (Attachment as a bidentate would be expected to produce the di-iodo complex).

The reactions of $\text{Co}(\text{t} [14] \text{ diene})^{2+}$ with halogen radical anions are all fast (Table 11.6B) and may be diffusion controlled. The rate of solvent exchange on the tetragonally distorted $\text{Co}(\text{II})$ low spin d^7 complex is not known but by analogy with other tetragonally distorted systems ($\text{Cu}^{2+}_{\text{aq}}$, $\text{Cu}(\text{t} [14] \text{ diene})^{2+}$, $\text{Cr}^{2+}_{\text{aq}}$) the rate may be as high as 10^{10} s^{-1} . Rilemma and Endicott (1972) have studied the rates of reaction of various known outer sphere oxidants with $\text{Co}(\text{t} [14] \text{ diene})^{2+}$ and found a linear free energy relationship. From our calculated E^0 values for the halogen radical anions, assuming that the derived free energy relationship is applicable, the rate constants for outer sphere reactions of halogen radical anions with $\text{Co}(\text{t} [14] \text{ diene})^{2+}$ can be predicted. The values obtained are:

Cl_2^- , $3 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$; Br_2^- , $7 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$; I_2^- , $7 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$. I_2^- ($k_{\text{obs}} = 7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) reacts 10^5 times faster than predicted for an outer sphere reaction suggesting that this mechanism is inapplicable. Br_2^- ($k_{\text{obs}} = 1.45 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) reacts at almost the predicted rate and Cl_2^- ($k_{\text{obs}} = 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) reacts considerably slower than predicted but may be limited by the rate of diffusion. The observed correlations are not inconsistent with an outer sphere mechanism for the reaction of Br_2^- and Cl_2^- with $\text{Co}(\text{t}14\text{diene})^{2+}$ however the reaction of I_2^- is apparently inner sphere.

These considerations do not rule out the possibility of an inner sphere mechanism for Cl_2^- and Br_2^- . Unequivocal designation of the mechanism cannot be made until initial products have been characterized. Malone & Endicott (1972) made no product observation but wrote the reactions as inner sphere.



The reported reduction of $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$ by I_2^- (Malone & Endicott, 1972) proceeds at a rate many times faster than the rate of substitution on the Co (III) reactant and it is clear that this reaction must be outer sphere.

SECTION 12 - EXPERIMENTAL

The construction and performance of the flash photolysis apparatus has been described in sections 2.1.1 and 2.2. The source of most reagents has already been given in 2.6.1. The additional reagents for study of the redox reactions are discussed in 12.1.

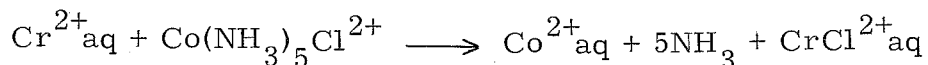
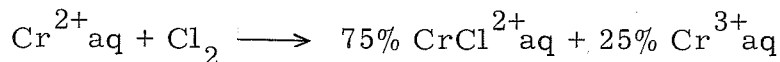
12.1 REAGENTS

Ferrous perchlorate solutions were prepared by reducing an acid solution of Fluka ferrous perchlorate electrolytically at a platinum cathode or with zinc amalgam. The presence of ferric ions was detected spectrophotometrically with concentrated ammonium thiocyanate solution. In a freshly prepared 0.1 mol l^{-1} solution of $\text{Fe}^{2+}_{\text{aq}}$ in 0.1 mol l^{-1} perchloric acid ferric concentrations of $<10^{-5} \text{ mol l}^{-1}$ could be achieved. Solutions were prepared and stored under a nitrogen atmosphere.

Iron (III) perchlorate, cobalt (II) perchlorate, manganese (II) perchlorate, nickel (II) perchlorate and copper (II) perchlorate solutions were prepared from Fluka salts without further purification.

Chromium (III) perchlorate was either prepared by the method of Espenson (1964) or obtained from G. F. Smith Chemicals. Chromium (II) perchlorate solutions were prepared by reducing chromium (III) perchlorate solutions electrolytically at a mercury cathode or with zinc amalgam. Preparation and storage was performed under a nitrogen atmosphere.

Solutions of chloropentaaquochromium (II) perchlorate were prepared by reaction of $\text{Cr}^{2+}_{\text{aq}}$ with chlorine or with chloropentaammine cobalt (III) dichloride in deaerated solution.



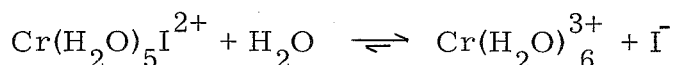
Separation from other products was achieved in a Sephadex CM ion

exchange column. The desired dipositive ion was eluted with 0.2 mol l^{-1} perchloric acid.

Bromopentaaquochromium (III) solutions were prepared in a similar manner by reacting chromium (II) perchlorate solutions with bromine or bromopentaamminecobalt (III) dibromide, followed by ion exchange separation.

Halogenopentaamminecobalt (III) dihalides were prepared by oxidising a solution containing the halogenopentaamminecobalt (II) ion with hydrogen peroxide.

Iodopentaaquochromium (III) perchlorate which rapidly aquates to hexaaquochromium (III) ($t_{\frac{1}{2}} \sim 20 \text{ min}$ at 25°C ; Espenson, 1964),



was prepared in solution by reacting chromium (II) with a cold de-aerated iodine solution and removing excess iodine by extraction with carbon tetrachloride. The spectra of monohalogenochromium (III) complexes are shown in Fig. 12.1A.

Zinc (II) perchlorate was prepared by neutralizing perchloric acid with zinc carbonate and recrystallized from perchloric acid.

Vanadium (II) perchlorate solutions were prepared by reducing vanadium (IV) perchlorate solutions with zinc amalgam. It was prepared and stored under nitrogen. Vanadium (IV) solutions were prepared by double decomposition of vanadyl sulphate (BDH) and barium perchlorate (BDH). The precipitated barium sulphate was removed by centrifugation.

Zinc amalgams were prepared from BDH Anala R zinc and triple distilled mercury.

12.2 Analysis and standardization

Iron (II), chromium (II) and vanadium (II) solutions were usually standardized by titration with primary standard AR potassium permanganate. In very dilute solution ($<10^{-2} \text{ mol l}^{-1}$), ferrous was

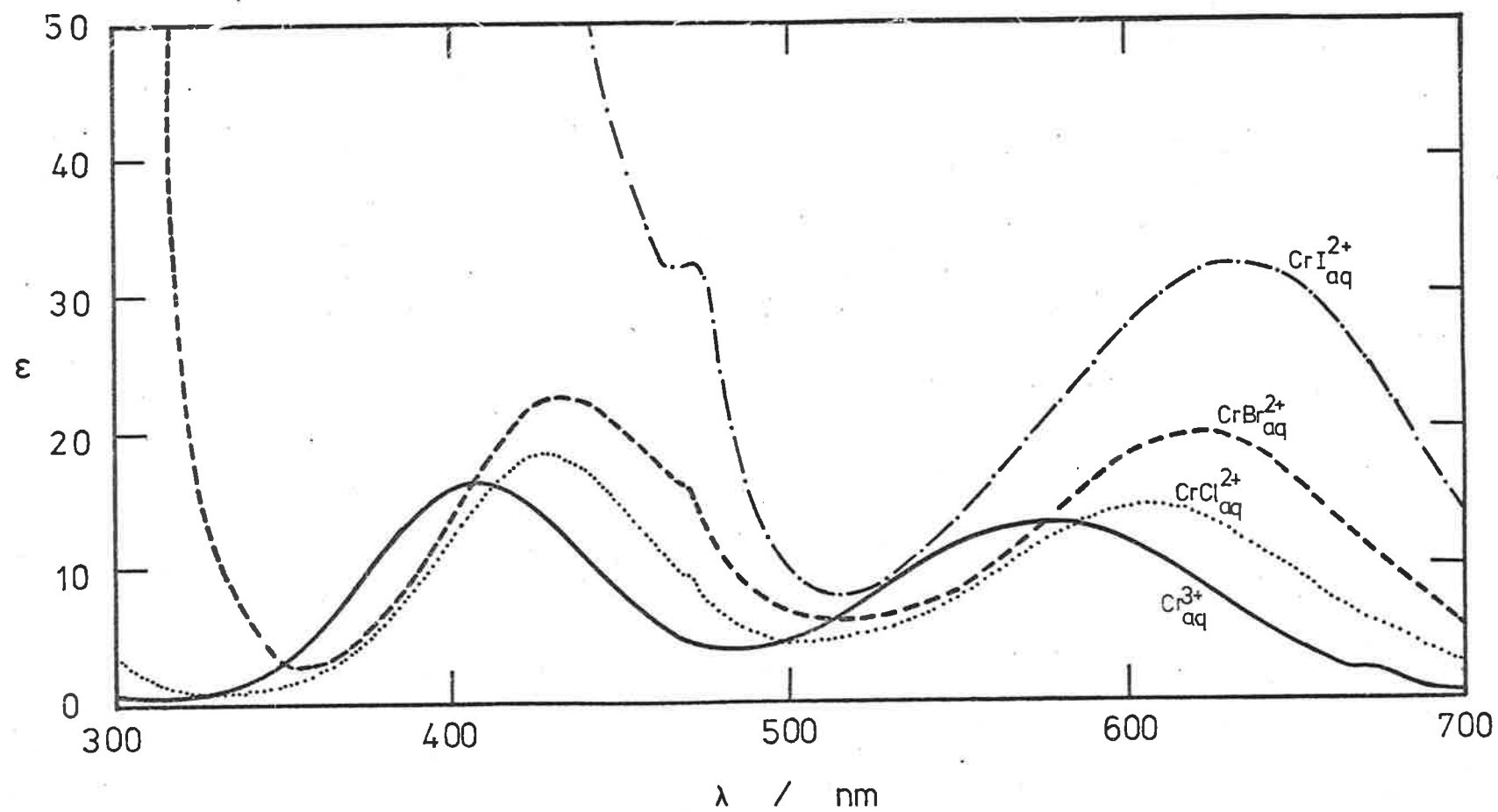


Fig. 12.1A Spectra $\text{Cr(H}_2\text{O)}_6^{3+}$

determined spectrophotometrically with o-phenanthroline (Vogel, 1962) and chromous was determined by addition to a standard iodine solution prepared from potassium iodide and primary standard potassium iodate (excess iodine was titrated with thiosulphate).

Manganese (II) was determined by potentiometric titration with permanganate in pyrophosphate medium. (Vogel, 1962)

Cobalt (II), nickel (II) and copper (II) were analyzed by electrodeposition of the metal. The presence of ~ 2% cobalt in the nickel solution was detected by atomic absorption spectroscopy.

Iron (III) and zinc (II) were determined by potentiometric titration with AR sodium ethylenediaminetetraacetic acid.

Chromium (III) was determined spectrophotometrically as chromate after oxidation with alkaline hydrogen peroxide.

12.3 METHODS

The methods used in flash photolysis have been previously described (Section 2.7). The same methods were used to study redox reactions of halogen radical anions. Air sensitive solutions of metal ions were added to the appropriate halide solution after deaeration.

γ irradiations were carried out with a 1000 Ci ^{60}Co source. Standard ferrous sulphate dosimetry was used.

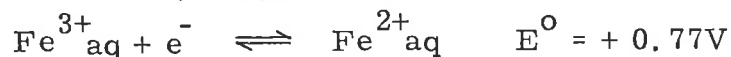
SECTION 13 - REDOX REACTIONS

Reactions of halogen radical anions Cl_2^- , Br_2^- and I_2^- with divalent transition metal aquo ions vanadium through zinc have been investigated. The reactions of Cr^{2+}aq and V^{2+}aq were not suitable for quantitative investigation using flash photolysis because of the rapidity of the reactions. The rates of these reactions have been determined by my supervisor Dr. G.S. Laurence. The results which have yet to be published are included in 13.7 and 13.8.

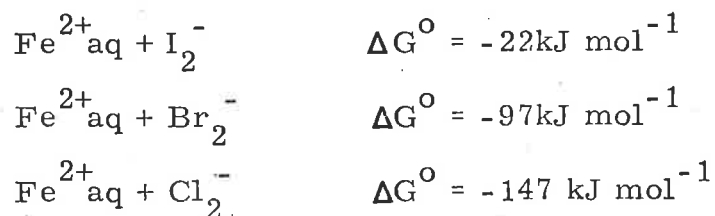
The various metal ions are discussed in an order which allows logical development of mechanistic arguments.

13.1 IRON (II)

In acid solution the potential of the ferric-ferrous half cell is +0.77 V (Latimer, 1950)



All three radical anions are sufficiently strong oxidising agents to oxidise iron (II) (see Table 11.6A), the free energy changes for the reactions being

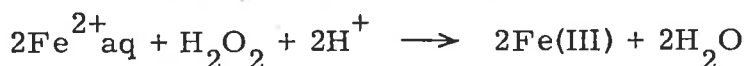


The reaction between Fe^{2+}aq and I_2^- has been studied by Laurence (to be published) and will be considered only in comparison with the other radical anions.

Iron (II) reacts rapidly with chlorine and bromine (Conocchioli, Hamilton & Sutin, 1965; Carter & Davidson, 1952).



and hydrogen peroxide (Wells, 1969).



Consequently production of halogen radical anions by flash photolysis or pulse radiolysis of solutions containing halogens or hydrogen peroxide, in the presence of ferrous, is impractical. (cf Sections 2.3.2, 2.3.4).

Production of X_2^- by flash photolysis of nitrous oxide saturated dilute solutions of halide ions (2.3.1) suffers from the disadvantages that:

- (a) for N_2O to be an efficient electron scavenger (Section 4.3.2) the pH must be greater than 4 and at this pH ferrous is difficult to store and prepare;
- (b) in chloride solutions ferrous acts as an efficient inner filter (see Section 5.1) and yields of Cl_2^- are very small ($\sim 10^{-7} \text{ mol l}^{-1}$). Addition of small ($10^{-3} - 10^{-4} \text{ mol l}^{-1}$) concentration of ferric ion; to ferrous, halide solution produces equilibrium concentrations of monohalogenoiron (III) complexes ($10^{-4} - 10^{-5} \text{ mol l}^{-1}$) which are photo-active and produce relatively large ($\sim 5 \times 10^{-6} \text{ mol l}^{-1}$) concentrations of X_2^- (see Section 2.3.3).



Preliminary experiments showed that in both bromo and chloro systems the observed rate constants for disproportionation of X_2^- produced by flash photolysis of a solution containing ferric ions, halide ions and acid were in good agreement with values obtained in other systems (see 5.3.9, 4.3.9).

Except where indicated all flash photolysis experiments were performed in ferric halide solutions.

13.1.1 Rates and temperature dependence $\text{Fe}^{2+}_{\text{aq}} + \text{X}_2^-$

In acid solution (pH 1, $I = 0.2 \text{ mol l}^{-1}$), Br_2^- and Cl_2^- react with ferrous ions.

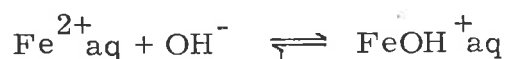


The rates were studied over the range 15 - 40°C and activation parameters determined. Table 13.1A lists the derived rate and activation energy data.

Table 13.1A

	$\text{Fe}^{2+} + \text{Br}_2^-$	$\text{Fe}^{2+} + \text{Cl}_2^-$
k_{25} ($\text{l mol}^{-1} \text{s}^{-1}$)	$(3.6 \pm 0.4) \times 10^{6*}$	$(1.4 \pm 0.2) \times 10^7$
$\Delta H^\ddagger$ (kJ mol^{-1})	(25.2 ± 2)	(26.5 ± 2)
$\Delta S^\ddagger$ ($\text{J mol}^{-1} \text{K}^{-1}$)	(-42 ± 12)	(-20 ± 12)

Notes: * The apparent contradiction with the value of $8.6 \times 10^6 \text{ l mol}^{-1} \text{s}^{-1}$ (Thornton & Laurence, 1970) arises from pH differences. The earlier work was performed at pH6 where significant hydrolysis of ferrous takes place.

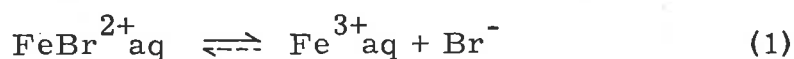


It is proposed that FeOH^+ reacts considerably faster with Br_2^- than does $\text{Fe}^{2+}_{\text{aq}}$. The increase in rate at pH6 is due to participation of FeOH^+ in the overall reaction.

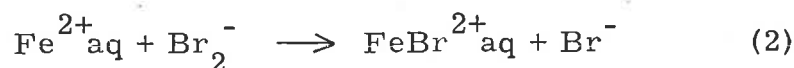
13.1.2 Mechanism $\text{Fe}^{2+}_{\text{aq}} + \text{Br}_2^-$

Flash photolysis of an N_2O saturated solution of ferrous and bromide produces a small but relatively long lived ($t_{1/2} \sim \text{ms}$) transient absorption (Thornton & Laurence, 1970). The spectrum and rate of disappearance of this species have been measured. The spectrum is

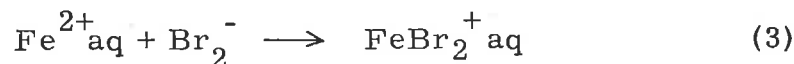
very similar to the spectrum of $\text{Fe}(\text{H}_2\text{O})_5\text{Br}^{2+}$ obtained in solutions of ferric and bromide ions (see Fig. 13.1A) and the rate of disappearance corresponds to the expected rate of aquation of the complex under the experimental conditions. (Carlyle & Espenson, 1969; Matthies & Wendt, 1961).



This absorption is assigned to $\text{FeBr}^{2+}_{\text{aq}}$. The yield of $\text{FeBr}^{2+}_{\text{aq}}$ roughly corresponds to that of Br_2^- produced by the flash, when the concentration of ferrous is sufficiently high to capture all Br_2^- in competition with the disproportionation reaction of Br_2^- .

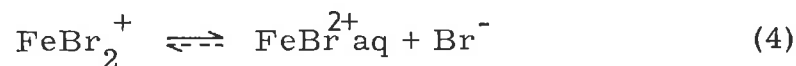


The experimental observations are not sufficiently accurate to rule out the possibility that the disubstituted ferric complex is initially formed (Reaction (3))



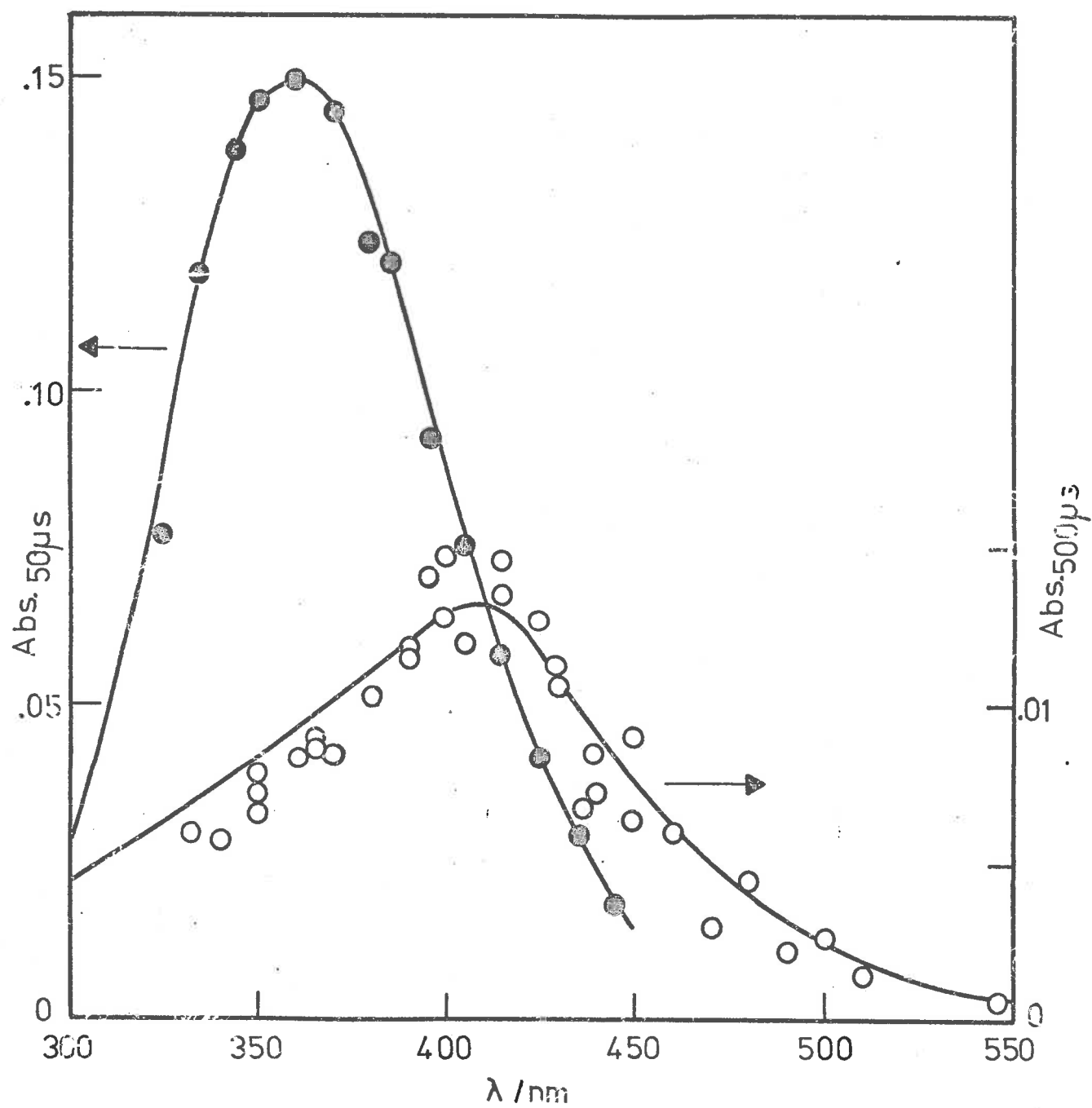
because although the spectrum of FeBr_2^+ is not accurately known, it is probable that it is little different from that of $\text{FeBr}^{2+}_{\text{aq}}$.

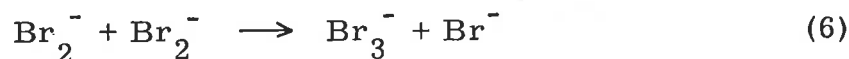
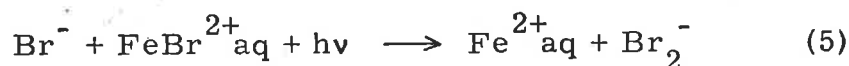
Consequently the absorbance change accompanying reaction (4) maybe small and undetectable.



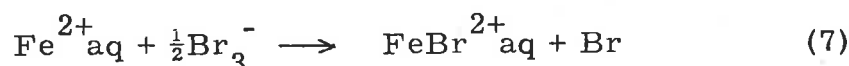
Flash photolysis of solutions containing the monobromoferric ion under conditions where only this species is photolyzed (a filtered light flash with $\lambda > 270$ nm was used) supports the proposed 1:1 stoichiometry. Absorbance changes in a solution without ferrous ion are shown in Fig. 13.1B, as are changes in the presence of sufficient ferrous ($\sim 10^{-2} \text{ mol l}^{-1}$) to scavenge all Br_2^- . In the absence of ferrous the optical density does not immediately return to its initial value on disappearance of Br_2^- , but due to removal of some $\text{FeBr}^{2+}_{\text{aq}}$ in the light flash, the solution becomes less absorbing.

Fig. 13.1A Experimental Spectra of Br_2^- , $\bullet$; $\text{FeBr}^{2+}_{\text{aq}}$, $\circ$.
Previously Reported Spectra, — .

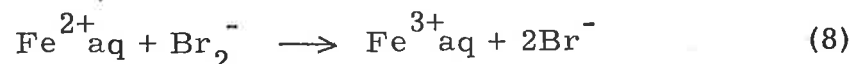
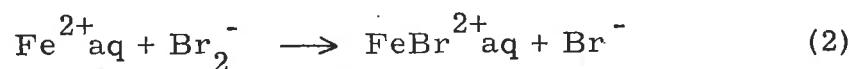




A much slower ($t_{1/2}$ ~ seconds) redox reaction between Br_3^- and $\text{Fe}^{2+}_{\text{aq}}$ (Reaction 7) restores the absorbance to its initial value.



In the presence of excess ferrous, Br_2^- does not disproportionate (Reaction 6) but reacts with $\text{Fe}^{2+}_{\text{aq}}$ by either reaction (2) or (8).



In the event of reaction (2) being the preferred path an exactly equivalent amount of $\text{FeBr}^{2+}_{\text{aq}}$ is removed (5) and reformed (2), and the absorbance returns to its initial value on disappearance of Br_2^- . If $\text{Fe}^{2+}_{\text{aq}}$ reacts with Br_2^- by reaction (8) the absorbance on disappearance of Br_2^- would be less than the initial value. At 366 nm where neither $\text{Fe}^{2+}_{\text{aq}}$ or $\text{Fe}^{3+}_{\text{aq}}$ or Br_3^- absorb significantly it would be the same, within experimental error, as the absorbance in the absence of $\text{Fe}^{2+}_{\text{aq}}$ (see Fig. 13.1B).

Small discrepancies in return to the initial absorbance can be detected and this experiment is a sensitive probe to determine the amount of Br_2^- reacting by (2) or (8). The absorbance changes in the presence of excess $\text{Fe}^{2+}_{\text{aq}}$ are shown in Fig. 13.1B. Within the limits of experimental error the absorbance at 366 nm returns to its initial value on disappearance of Br_2^- , which must react with $\text{Fe}^{2+}_{\text{aq}}$ solely by reaction (2).

The observation that the initial product is 100% $\text{FeBr}^{2+}_{\text{aq}}$ unequivocally defines the mechanism as inner sphere (see 11.4.2) In the absence of observation of intermediates classification into the categories "inner sphere electron transfer controlled" and "inner sphere substitution controlled" (see 11.3.2) can be accomplished by

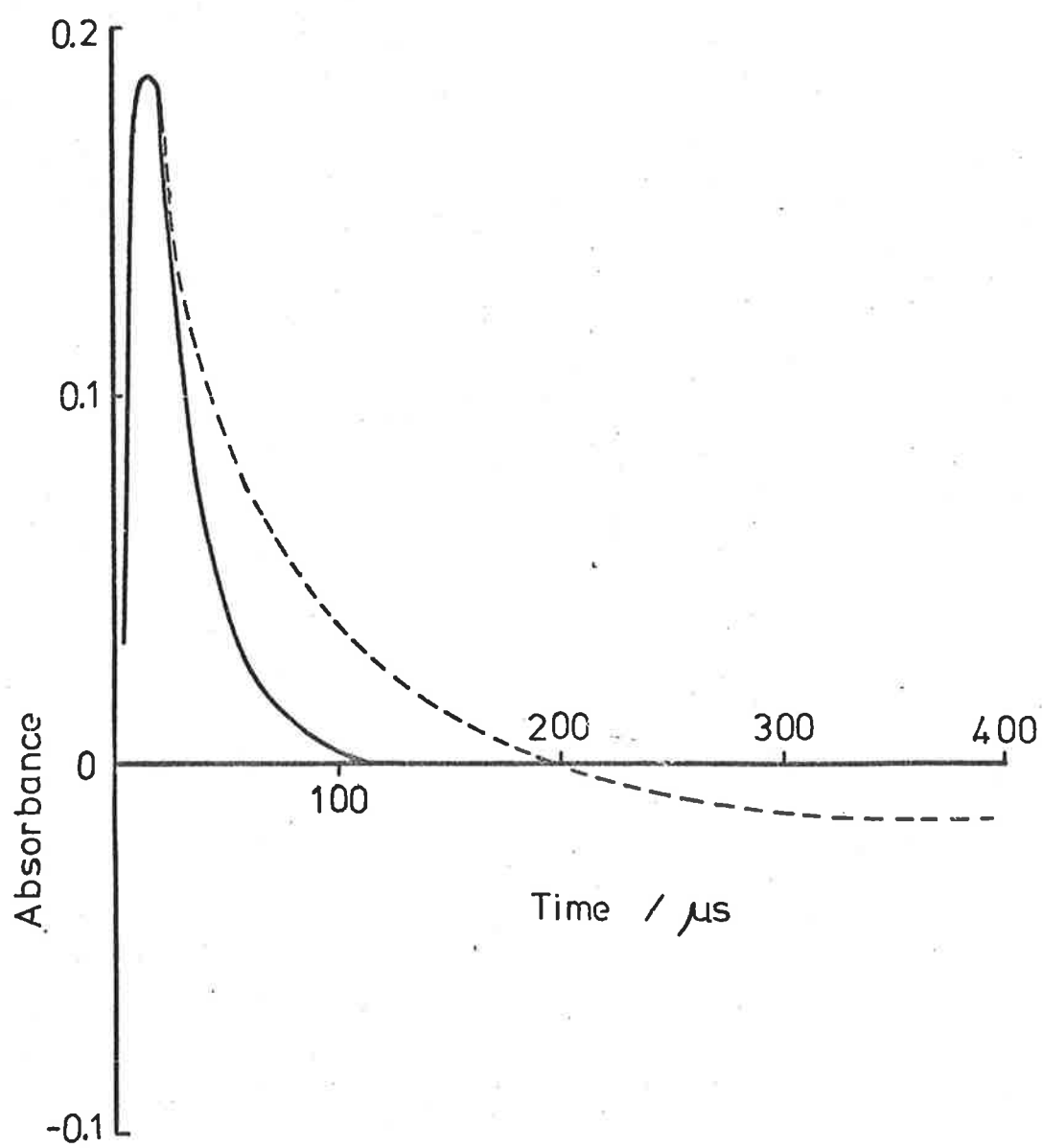


Fig. 13.1B Flash Photolysis of $\text{FeBr}^{2+}_{\text{aq}}$.
 (-----, No $\text{Fe}^{2+}_{\text{aq}}$; ———, $[\text{Fe}^{2+}_{\text{aq}}] = 2 \times 10^{-2} \text{ mol l}^{-1}$)

comparison of substitution rates with redox rates. The rate constant, k_{ex} , for solvent exchange (11.1.1) on $\text{Fe}^{2+}_{\text{aq}}$ ions is $\approx 3.2 \times 10^6 \text{ s}^{-1}$ (Swift & Connick, 1962), assumption of the Eigen mechanism for substitution of an anion (Br_2^-) through an ion pair leads to the relation:

$$k_{\text{sub}} = \frac{6}{8} K_{\text{IP}} \cdot k_{\text{ex}} \quad (11.1.3)$$

If the redox reaction is substitution limited then

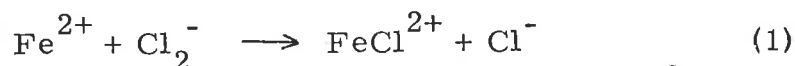
$$k_{\text{redox}} = k_{\text{sub}} \text{ and,}$$

$$k_{\text{redox}} = \frac{6}{8} K_{\text{IP}} \cdot k_{\text{ex}}$$

Substituting values of k_{redox} and k_{ex} one obtains $K_{\text{IP}} = 1.5$, a value which is quite reasonable for ion pair formation between a $2+$ cation ($\text{Fe}^{2+}_{\text{aq}}$) and a relatively large $1-$ anion (Br_2^-) (Fuoss, 1958; Eigen, 1954). The evidence is that the reaction of ferrous with Br_2^- proceeds by an inner sphere substitution controlled mechanism.

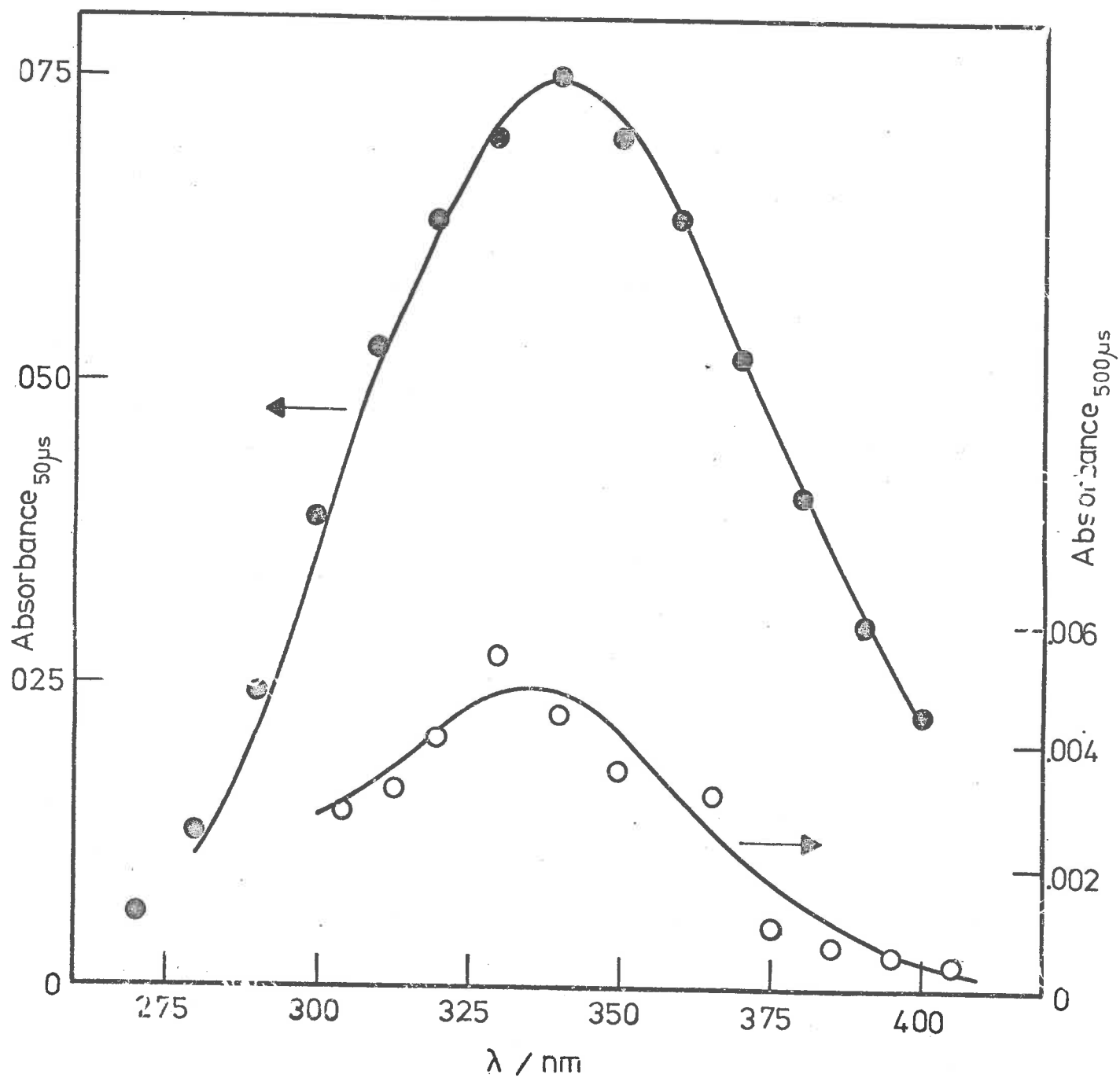
13.1.3 Mechanism $\text{Fe}^{2+}_{\text{aq}} + \text{Cl}_2^-$

Flash photolysis of a solution containing chloride and $\text{Fe}^{2+}_{\text{aq}}$ at pH1 produces Cl_2^- ($\sim 10^{-7} \text{ mol l}^{-1}$) which rapidly decays to form a relatively long lived transient species with the spectrum shown in Fig. 13.1C. A close similarity with the spectrum of $\text{FeCl}^{2+}_{\text{aq}}$ is observed. The decay of this species was first order with a rate constant of 40 s^{-1} in good agreement with that expected for aquation of chloropentaaquoferrous ions under the experimental conditions (37 s^{-1} ; Moorhead & Sutin, 1967).



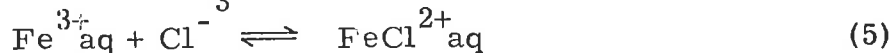
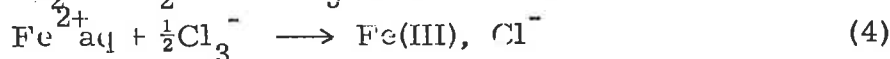
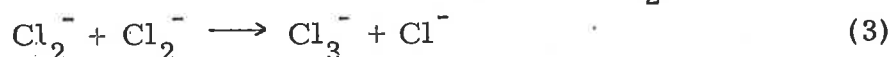
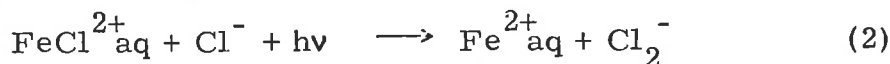
The stoichiometry for the formation of $\text{FeCl}^{2+}_{\text{aq}}$ from Cl_2^- can only be obtained by comparison of the amount of Cl_2^- formed in the absence of $\text{Fe}^{2+}_{\text{aq}}$ and the amount of $\text{FeCl}^{2+}_{\text{aq}}$ formed in the presence of $\text{Fe}^{2+}_{\text{aq}}$, because under conditions where the concentration of ferrous is sufficiently large to capture all Cl_2^- the rate of decay of Cl_2^- is too

Fig. 13.1C Experimental spectra of Cl_2^- , $\bullet$; $\text{FeCl}^{2+}_{\text{aq}}$, $\circ$.
Previously Reported Spectra, —.

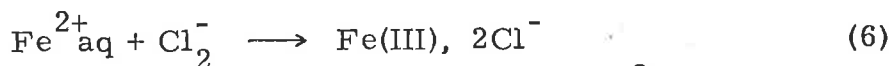


great to give an accurate measure of the initial Cl_2^- concentration. If one assumes that the Cl_2^- yield is the same in the presence and absence of $\text{Fe}^{2+}_{\text{aq}}$ the approximate yield of $\text{FeCl}^{2+}_{\text{aq}}$ is $40 \pm 20\%$ of the Cl_2^- yield indicating that reaction (1) may not be the only significant reaction.

Flash photolysis of solutions of ferric ion and chloride, under conditions where no Cl^- is photolysed ($\lambda > 220 \text{ nm}$), produces changes shown in Fig. 13.1D. The following scheme, which is analogous to that proposed for Br_2^- , is consistent with the observed absorbance changes at 366 nm.



Addition of $\text{Fe}^{2+}_{\text{aq}}$ in sufficient concentration ($\sim 10^{-2} \text{ mol l}^{-1}$) to remove all Cl_2^- in competition with reaction (3) results in the absorbance changes shown in Fig. 13.1D. These differ from the absorbance changes shown by the corresponding bromide system (Fig. 13.1B) where return to the initial absorbance occurs simultaneously with removal of Br_2^- . It is clear that the ratio of $[\text{FeCl}^{2+}]$ removed by the flash to $[\text{FeCl}^{2+}]$ reformed by reaction (6) is greater than 1.



The experiments in the absence of $\text{Fe}^{2+}_{\text{aq}}$ show a 1:1 stoichiometry between Cl_2^- formed and $\text{FeCl}^{2+}_{\text{aq}}$ the absorbance eventually returns to its initial value with a rate consistent with that for re-equilibration of reaction (5). The exact return to the initial absorbance implies that a 1:1 stoichiometry exists between $\text{FeCl}^{2+}_{\text{aq}}$ removed (2) and Fe(III) reformed (6) on removal of Cl_2^- . The results indicate that a 1:1 stoichiometry between Cl_2^- removed and $\text{FeCl}^{2+}_{\text{aq}}$

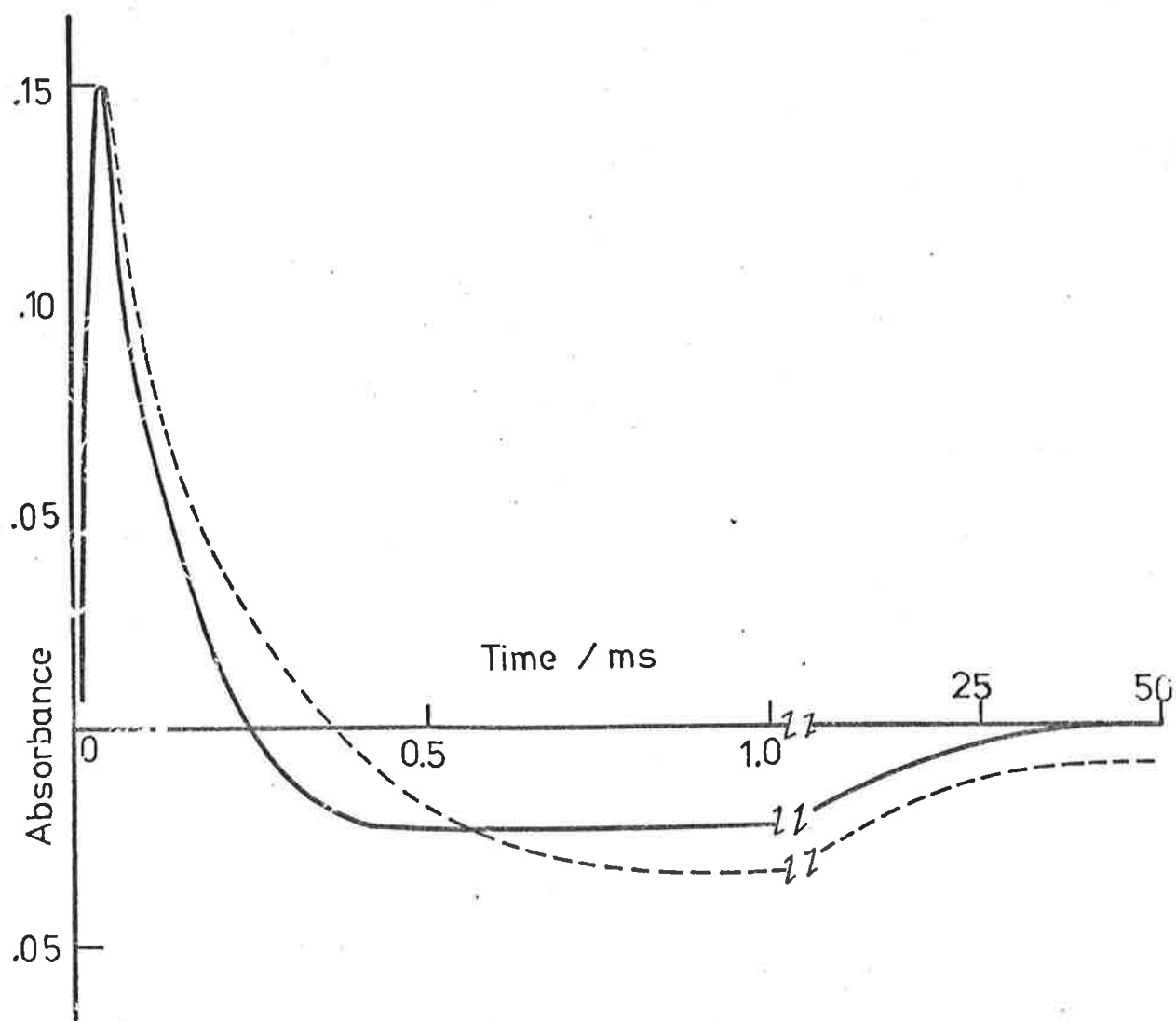
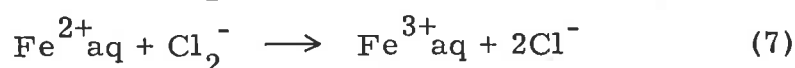


Fig. 13, 1D Flash Photolysis of $\text{FeCl}^{2+}_{\text{aq}}$.
 (-----, No $\text{Fe}^{2+}_{\text{aq}}$; ———, $[\text{Fe}^{2+}_{\text{aq}}] = 10^{-2} \text{ mol l}^{-1}$)

reformed does not exist. Reaction (6) must be composed of two paths.



A measure of the relative magnitudes of k_1 and k_7 can be obtained if the amount of $\text{FeCl}^{2+}_{\text{aq}}$ removed (equivalent to total ferric reformed) and the amount of $\text{FeCl}^{2+}_{\text{aq}}$ directly reformed (Reaction 1) can be measured. This ratio, numerically equal to $(k_1 + k_7)/k_1$, and the total rate of removal of Cl_2^- i. e. k_6 or $(k_1 + k_7)$ can be used to calculate the absolute magnitudes of k_1 and k_7 . Measurement of k_1 and k_7 at various temperatures gives the Arrhenius activation parameters listed in Table 13.1B.

Table 13.1B

$\text{Fe}^{2+}_{\text{aq}} + \text{Cl}_2^-$ Activation parameters

Reaction	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$k_{25^\circ\text{C}}$
	kJ mol^{-1}	$\text{J mol}^{-1}\text{K}^{-1}$	$\text{l mol}^{-1}\text{s}^{-1}$
(1)	31.5 ± 4	-21 ± 15	$(4.0 \pm 0.6) \times 10^6$
(7)	22.7 ± 4	-36 ± 15	$(1.0 \pm 0.2) \times 10^7$
Difference	$+8.8 \pm 4$	$+15 \pm 15$	

Although the overall uncertainties in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are as large as the difference between k_1 and k_7 , the difference terms $(\Delta H^\ddagger_1 - \Delta H^\ddagger_7)$ and $(\Delta S^\ddagger_1 - \Delta S^\ddagger_7)$ are known with more precision (see Table 13.1B). There is no doubt that the percentage of reaction going by path (1) increases as the temperature is raised, therefore $\Delta H^\ddagger_1 > \Delta H^\ddagger_7$ and similarly $\Delta S^\ddagger_1 > \Delta S^\ddagger_7$.

The initial products of reactions (1) and (7) are $\text{FeCl}^{2+}_{\text{aq}}$ and $\text{Fe}^{3+}_{\text{aq}}$ respectively. The mechanisms for these paths can be

unequivocally designated "inner sphere" and "outer sphere". The inner sphere path has a rate constant k_1 of $4 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$, close to the limit expected for a substitution controlled reaction. (cf 13.1.2)

Reaction of $\text{Fe}^{2+}_{\text{aq}}$ with Cl_2^- must proceed by concurrent "inner sphere substitution controlled" and "outer sphere" paths.

13.1.4 Effect of varying X_2^-

The rate constants for the reactions of Cl_2^- and Br_2^- with $\text{Fe}^{2+}_{\text{aq}}$ can be compared with the values of Laurence for the reaction of I_2^- . (See Table 13.1C).

An initial product of the $\text{Fe}^{2+}_{\text{aq}}, \text{I}_2^-$ reaction was not observed, but this does not rule out the possibility of an inner sphere mechanism for this reaction as in a thorough stopped flow investigation of the $\text{Fe}^{3+}_{\text{aq}}, \text{I}^-$ reaction, thought to also proceed through the inner sphere $\text{FeI}^{2+}_{\text{aq}}$ complex (see 13.1.6), Ellis and Laurence (1972) also failed to observe $\text{FeI}^{2+}_{\text{aq}}$.

The difference in ΔG^0 for the reactions of $\text{Fe}^{2+}_{\text{aq}}$ with I_2^- and Cl_2^- is 126 kJ mol^{-1} . Assuming that the Marcus relationship ($\Delta G^\ddagger \approx 0.5 \Delta G^0$) holds for the outer sphere reactions of $\text{Fe}^{2+}_{\text{aq}}$ with X_2^- , the rate constant of an outer sphere $\text{Fe}^{2+}_{\text{aq}}, \text{I}_2^-$ reaction would be $< 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$. The observed rate constant is 10^{10} times greater and it is improbable that the theoretical relation is so much in error. The mechanism of the $\text{Fe}^{2+}_{\text{aq}}, \text{I}_2^-$ reaction must be inner sphere rather than outer sphere. It is not surprising that only the Cl_2^- reaction shows any evidence of an outer sphere path, in view of the rates predicted by the Marcus relation.

Comparison of the three inner sphere rate constants and the rate constant of $3.2 \times 10^6 \text{ s}^{-1}$ for solvent exchange on $\text{Fe}^{2+}_{\text{aq}}$ (Swift and Connick, 1962) makes it certain that all three reactions are limited by the rate of substitution.

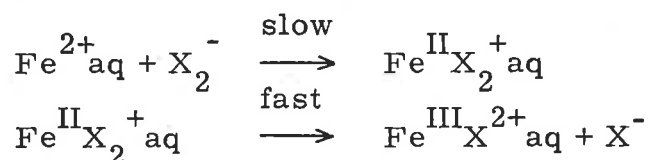
Table 13.1C

Rates and Mechanisms of $\text{Fe}^{2+}_{\text{aq}} + \text{X}_2^-$ Reactions

Reaction	$k_{25^\circ} \times 10^6$ ($\text{l mol}^{-1} \text{s}^{-1}$)	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ ($\text{J mol}^{-1} \text{K}^{-1}$)	Initial Product	Mech*
$\text{Fe}^{2+} + \text{Cl}_2^-$	(4.0 ± 0.6)	31.5 ± 4	-21 ± 15	FeCl^{2+}	IS
$\text{Fe}^{2+} + \text{Br}_2^-$	(3.6 ± 0.4)	25.2 ± 2	-42 ± 12	FeBr^{2+}	IS
$\text{Fe}^{2+} + \text{I}_2^-$	(3.6 ± 0.5)	-	-	?	?
$\text{Fe}^{2+} + \text{Cl}_2^-$	(10.0 ± 2)	22.7 ± 4	-36 ± 15	Fe^{3+}	OS

Notes: * IS = inner sphere

OS = outer sphere



13.1.5 Activation Parameters

No activation parameters were determined for the $\text{Fe}^{2+}\text{aq}, \text{I}_2^-$ reaction. Separation of the overall activation parameters for the $\text{Fe}^{2+}\text{aq}, \text{Cl}_2^-$ reaction into parameters for the inner sphere and outer sphere steps renders the individual values more uncertain than those for oxidation of Fe^{2+}aq by Br_2^- . Differences between the activation parameters for the inner sphere reaction of Fe^{2+}aq with Cl_2^- and Br_2^- may not be significant (see Table 13.1C). The reaction profile for a substitution controlled inner sphere reaction is shown in Appendix 3.2. The overall activation energy $\Delta H^\ddagger$ is given by

$$\Delta H^\ddagger = \Delta H_{\text{IP}}^{\text{O}} + \Delta H_{\text{sub}}^\ddagger$$

It is assumed that $\Delta H_{\text{sub}}^\ddagger$ is the same as $\Delta H_{\text{ex}}^\ddagger$ for solvent exchange if each process goes through a dissociative mechanism (see 11.1.3), implying that the presence of the incoming ligand in the second coordination sphere does not affect the rate of the dissociative step (i. e. the rate of solvent exchange in the ion pair is the same as that in the isolated aquo complex). The validity of this assumption is questionable (Hewkin and Prince, 1969).

Calculations of K_{IP} using the equation derived by Fuoss (1958) at various temperatures suggests that in aqueous solution $\Delta H_{\text{IP}}^{\text{O}}$ may be given by

$$+ \frac{9.7 Z_1 Z_2}{a} \text{ kJ mol}^{-1}$$

where $Z_1 Z_2$ is the reaction charge product

" a is the metal ligand distance in Å

For ion pair formation between M^{Z_1+}aq and $\text{X}_2^{Z_2-}$, $Z_1 Z_2 = -2$ and $2\text{Å}^{\text{O}} < a < 4\text{Å}^{\text{O}}$,

giving values of ΔH_{IP}° between -5 and -10 kJ mol^{-1} .

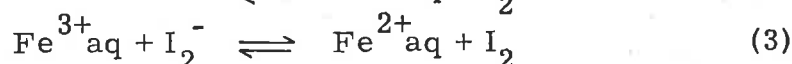
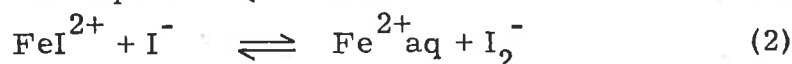
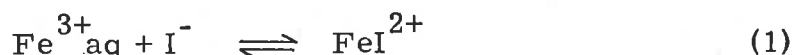
The best value for $\Delta H_{ex}^{\ddagger}$ on Fe^{2+}aq is $(35 \pm 4) \text{ kJ mol}^{-1}$ (Swift & Connick, 1962), $4 \pm 8 \text{ kJ mol}^{-1}$ larger than $\Delta H_{\ddagger}^{\ddagger}$ for the inner sphere reaction of Cl_2^- with Fe^{2+}aq and $(10 \pm 6) \text{ kJ mol}^{-1}$ larger than $\Delta H_{\ddagger}^{\ddagger}$ for reaction of Fe^{2+}aq with Br_2^- . These differences can be accommodated in ΔH_{IP}° . The measured activation parameters support the proposal that the inner sphere reactions of Cl_2^- and Br_2^- with Fe^{2+}aq are substitution controlled.

The relative values for the activation parameters of the inner and outer sphere Fe^{2+}aq , Cl_2^- reactions are given in Table 13.1B. The enthalpy of activation for the inner sphere path is at least 5 kJ mol^{-1} greater than that for the outer sphere path and the entropy of activation is at least $6 \text{ J mol}^{-1} \text{ K}^{-1}$ higher.

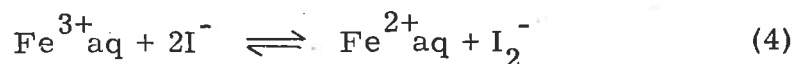
The extent of reorganization necessary to reach the transition state imposes the limit on the rate of a reaction. For an outer sphere reaction the reorganization involves precise adjustment of energy levels before electron transfer. This may involve entropy rather than enthalpy terms and can be contrasted with the inner sphere path where once substitution has taken place (an enthalpic barrier) little adjustment is likely to be necessary. A reaction exhibiting comparable inner and outer sphere paths might therefore be expected to have an outer sphere path with less enthalpy of activation but a more negative entropy of activation. The reaction of Fe^{2+}aq with Cl_2^- and other reactions with concurrent inner and outer sphere paths show this behaviour (Sykes and Thorneley, 1970; Newton and Baker, 1963; Nordmeyer and Taube, 1968).

13.1.6 Literature comparisons

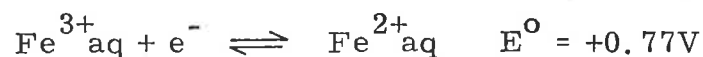
The reaction of Fe^{2+}aq with I_2^- has been proposed to account for retardation of the Fe^{3+}aq , I^- reaction by Fe^{2+}aq (Wagner, 1924; Fudge and Sykes, 1959; Hershey and Bray, 1936; Ellis and Laurence, 1972).



The reaction is second order in I^- so step (2) is probably rate limiting i. e. step (1) is a fast pre-equilibrium. A value for $k_2 \cdot k_1 / k_{-1}$ i. e. $k_2 K_1$ can be obtained from the measured rates; using the value of k_{-2} (see Table 13.1C) the free energy change for reaction (4) can be calculated.



The measurement of k_{-2} was performed at ionic strength of about 0.04 and 25°C . Hershey and Bray (1936) quote values of $k_4 = k_2 K_1$ of $87 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ at 0.09 mol l^{-1} and $810 \text{ l}^2 \text{ mol}^{-1} \text{ s}^{-1}$ at 0.0 mol l^{-1} ionic strength. A value of $\sim 200 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ can be estimated at an ionic strength of 0.04 mol l^{-1} . This gives $K_4 = 5 \times 10^{-5} \text{ l mol}^{-1}$ which corresponds to a free energy change of 25 kJ mol^{-1} or ΔE° of 0.25V . Combining this with E° for



one obtains

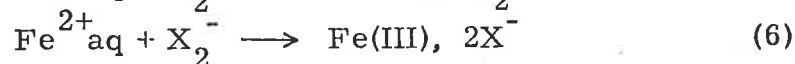
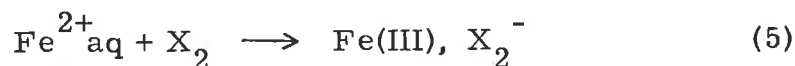


in excellent agreement with the value of $+1.00\text{V}$ calculated from thermodynamic quantities.

Fudge and Sykes (1959) found a ratio of 7 for k_{-2}/k_3 , although Ellis and Laurence (1972) found this to be applicable only over narrow concentration ranges. Using this value k_3 can be calculated as $5 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$. From the overall free energy change for the reaction (0.48V) and the free energy change for reaction (4) (0.25V), the free energy change for reaction (3) can be calculated to be $+0.73\text{V}$ corresponding to an equilibrium constant K_3 of $\sim 1.7 \times 10^{12}$. Hence the value of k_{-3} can be estimated as $\sim 3 \times 10^{-7} \text{ l mol}^{-1} \text{ s}^{-1}$.

The oxidations of $\text{Fe}^{2+}_{\text{aq}}$ by chlorine (Conocchioli, Hamilton

and Sutin, 1965) and bromine (Carter and Davidson, 1952) have been studied. The observed rate constants are $80 \pm 5 \text{ l mol}^{-1} \text{ s}^{-1}$ (Cl_2) and $\sim 30 \text{ l mol}^{-1} \text{ s}^{-1}$ (Br_2). Reduction of the halogen is assumed to proceed through the radical anion.

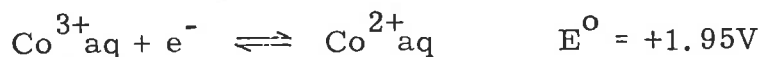


Investigation of the nature of the Fe (III) product in the Cl_2 reaction showed $\sim 70\%$ $\text{FeCl}^{2+}_{\text{aq}}$ and $\sim 30\%$ $\text{Fe}^{3+}_{\text{aq}}$. From the current work reaction (5) is known to produce $\sim 30\%$ $\text{FeCl}^{2+}_{\text{aq}}$ so that if reaction (5) produces 100% $\text{FeCl}^{2+}_{\text{aq}}$ the overall percentage of $\text{FeCl}^{2+}_{\text{aq}}$ produced would be $\sim 65\%$ in good agreement with the reported value. It is apparent that reaction (5) is inner sphere and comparison of the rate constant ($80 \text{ l mol}^{-1} \text{ s}^{-1}$) with the rate constant for solvent exchange on $\text{Fe}^{2+}_{\text{aq}}$ ($\sim 3 \times 10^6 \text{ s}^{-1}$) suggests that the reaction is not substitution limited.

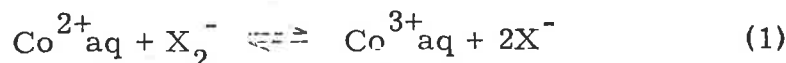
Product analysis on the $\text{Fe}^{2+}_{\text{aq}}$, Br_2 reaction was not possible but it is likely that reaction (5) ($\text{X} = \text{Br}$) is also "inner sphere electron transfer controlled", ($k \sim 30 \text{ l mol}^{-1} \text{ s}^{-1}$), reaction (6) ($\text{X} = \text{Br}$) is known to be 100% inner sphere and the only expected Fe(III) product must be $\text{FeBr}^{2+}_{\text{aq}}$.

13.2 COBALT (II)

In acid aqueous solution the potential of the cobaltic, cobaltous half cell is +1.95V (Johnson & Sharpe, 1964).



Only the Cl_2^- , Cl^- couple has sufficient free energy change to displace equilibrium (1) to the right.

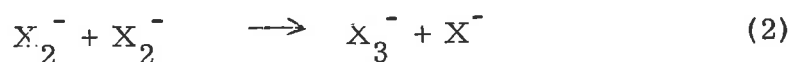
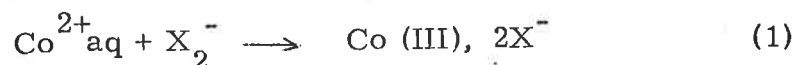




Cobalt (II) does not react with halogens or hydrogen peroxide and either of the systems Cl_2/Cl^- or $\text{H}_2\text{O}_2/\text{Cl}^-$ can be used to generate Cl_2^- in the presence of $\text{Co}^{2+}_{\text{aq}}$ (see 2.3.4).

13.2.1 $\text{Co}^{2+}_{\text{aq}} + \text{Br}_2^-$, I_2^-

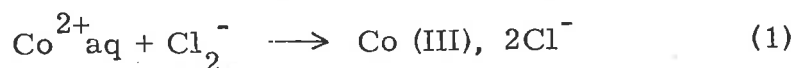
In bromine and iodine solution no reaction of $\text{Co}^{2+}_{\text{aq}}$ with Br_2^- or I_2^- could be observed. This may be because the equilibrium constant K_1 is unfavourable and/or the rate constant k_1 is too small to observe reaction (1) in competition with the disproportionation reaction (2).



If it is the magnitude of the rate constant which prevents observation of reaction (1) an estimated upper limit for k_1 is $10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

13.2.2 Rate and temperature dependence $\text{Co}^{2+}_{\text{aq}} + \text{Cl}_2^-$

$\text{Co}^{2+}_{\text{aq}}$ reacts with Cl_2^-



The rate constant, k_1 , was found to be independent of Co (II) concentration from $1 - 5 \times 10^{-2} \text{ mol l}^{-1}$ at 25°C . The temperature dependence ($15 - 40^\circ\text{C}$) of the rate constant gave the following results.

$$k_{25^\circ\text{C}} = (1.4 \pm 0.2) \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$$

$$\Delta H^\ddagger = 32 \pm 4 \text{ kJ mol}^{-1}$$

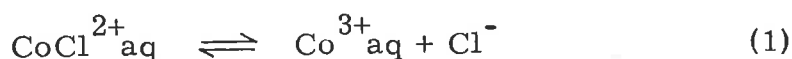
$$\Delta S^\ddagger = -29 \pm 12 \text{ J mol}^{-1} \text{ K}^{-1}$$

13.2.3 Mechanism $\text{Co}^{2+}_{\text{aq}} + \text{Cl}_2^-$

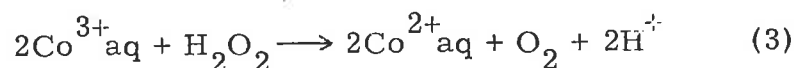
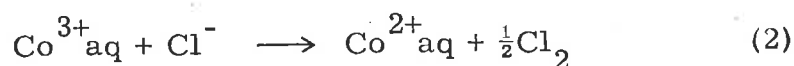
Reaction of Cl_2^- , from flash photolysis of hydrogen peroxide/chloride solutions, with $\text{Co}^{2+}_{\text{aq}}$ produces a relatively long lived ($t_{1/2} \sim 10\text{ms}$) transient with an absorption around 270 nm. The spectrum

of the transient is shown in Figure 13.2A. The spectra of $\text{CoCl}^{2+}_{\text{aq}}$ measured by stopped flow kinetics (McAuley, Malik and Hill, 1970) and that of $\text{Co}^{3+}_{\text{aq}}$ (Baxendale and Wells, 1957; Sutcliffe and Weber, 1960) are shown for comparison. When normalized to the same absorbance at 270 nm the spectrum of the transient shows good agreement with that of $\text{CoCl}^{2+}_{\text{aq}}$.

Figure 13.2B shows the variation of absorbance with time at 297 nm. The absorbance initially produced decays to about 1/3 of its initial value with $t_{\frac{1}{2}} \sim 10$ ms and then is more slowly restored to its initial value ($t_{\frac{1}{2}} \sim 50$ ms). The observed first order rate constant for the faster process is $59 \pm 2 \text{ s}^{-1}$ at 22°C in excellent agreement with a value of 57 s^{-1} extrapolated from the data of McAuley et al (1970) and a value of 30 s^{-1} at an ionic strength of 3.0 mol l^{-1} (Conocchioli, Nancollas and Sutin, 1965) for the rate of attainment of equilibrium (1)



The slower process is apparently a redox reaction of $\text{Co}^{3+}_{\text{aq}}$ with Cl^{-} or H_2O_2 (Wells and Husain, 1971) to restore the initial Co^{2+} .



The transient absorbing at 270 nm is $\text{CoCl}^{2+}_{\text{aq}}$ initially produced in excess of the equilibrium concentration by reaction (4)



From the re-equilibrium of $\text{CoCl}^{2+}_{\text{aq}}$ the formation constant K_{-1} is estimated to be $20 \pm 5 \text{ l mol}^{-1}$ in fair agreement with values of $26 \pm 3 \text{ l mol}^{-1}$ (Conocchioli et al, 1965) and $31 \pm 2 \text{ l mol}^{-1}$ (McAuley et al, 1970). The extinction coefficient of $\text{CoCl}^{2+}_{\text{aq}}$ was not measured by McAuley et al. Assuming a 1:1 stoichiometry between $\text{CoCl}^{2+}_{\text{aq}}$

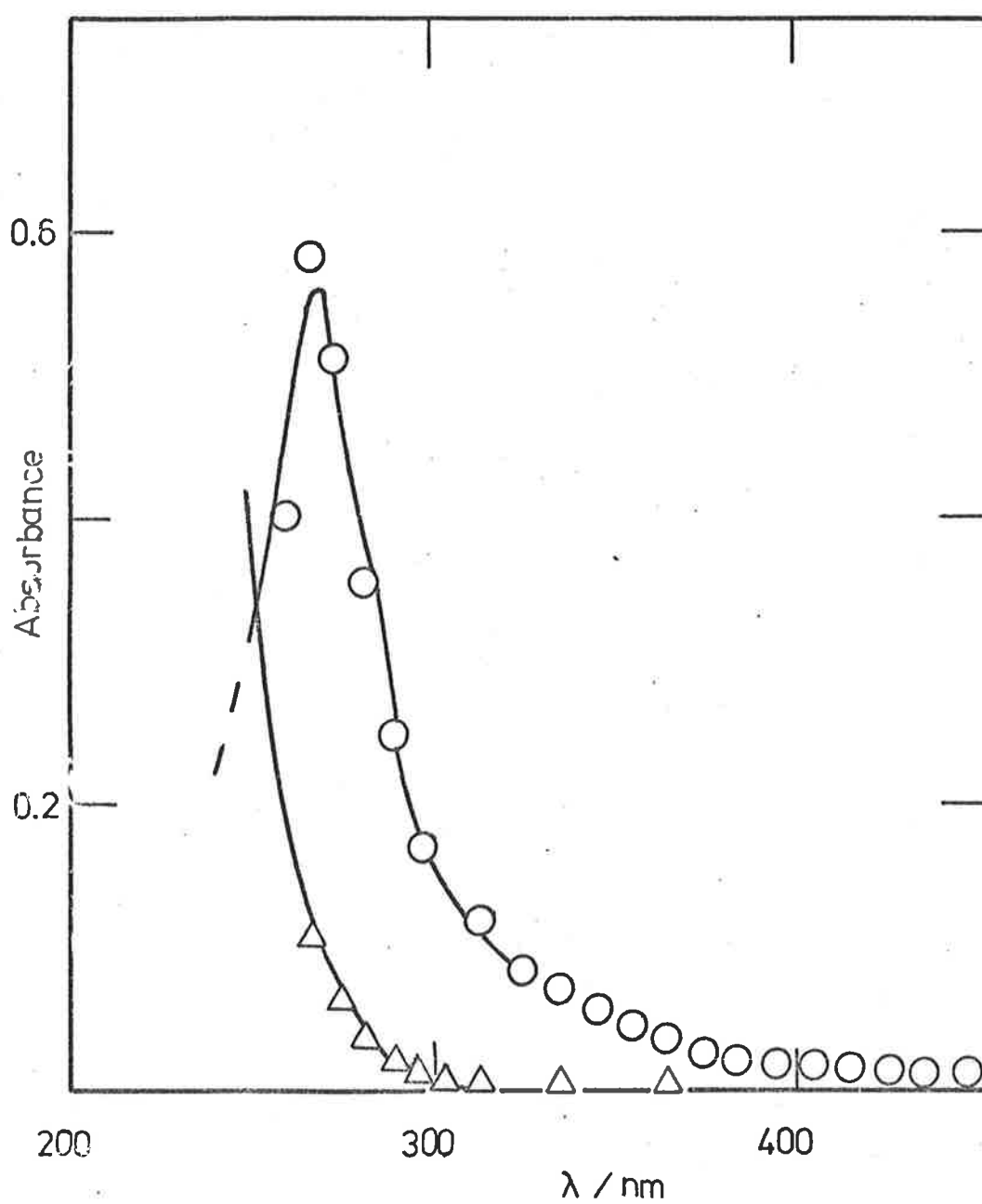


Fig. 13.2A Experimental Spectra of $\text{CoCl}^{2+}_{\text{aq}}$, $\bigcirc$; $\text{Co}^{3+}_{\text{aq}}$, $\triangle$.
Previously Reported Spectra, —

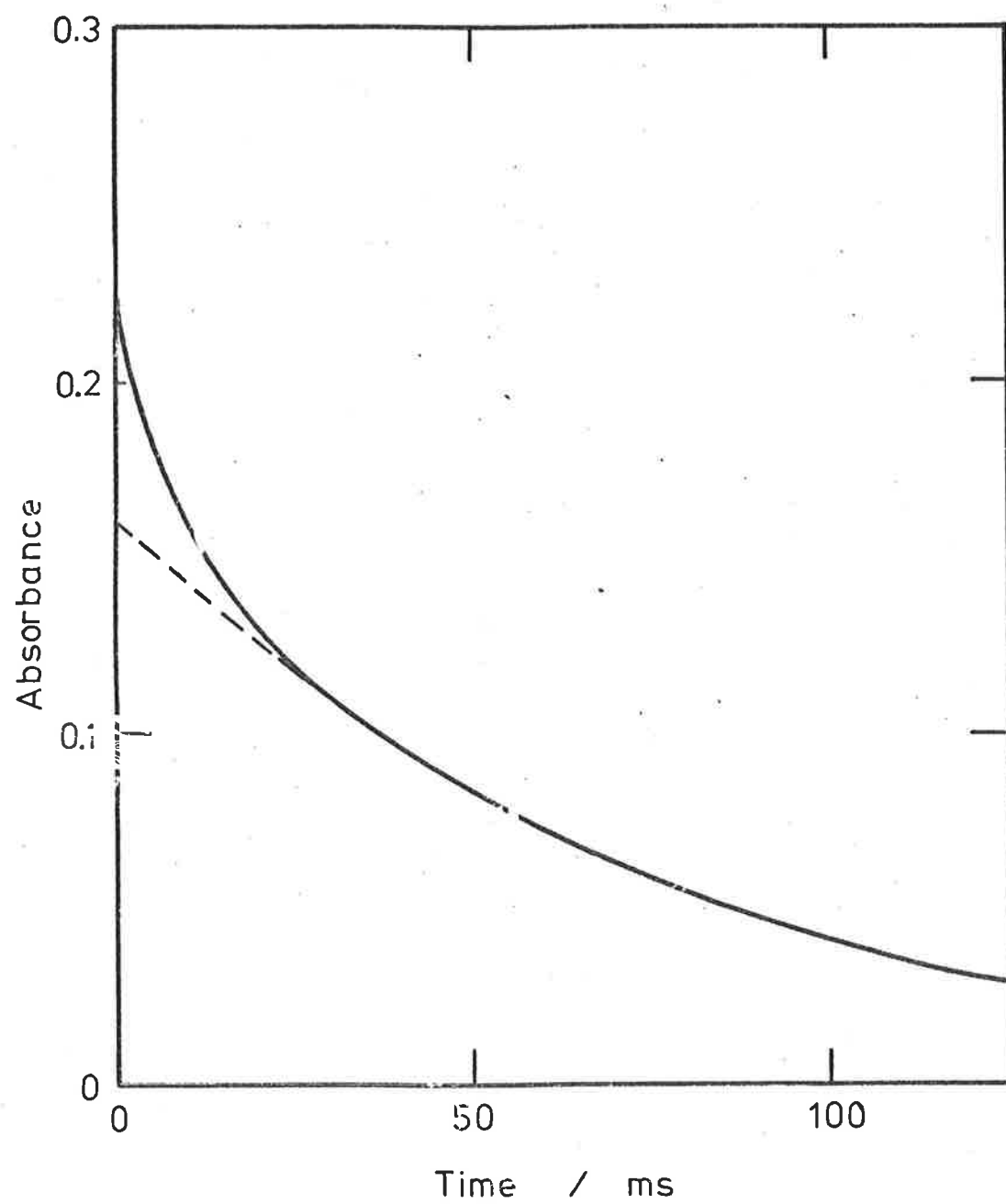


Fig. 13.2B $\text{Co}^{2+}_{\text{aq}} + \text{Cl}_2$. Variation of Absorbance with Time.

and Cl_2^- (reaction 4) the value is 5000 ± 2000 at 270 nm.

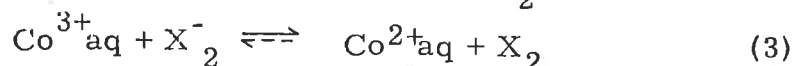
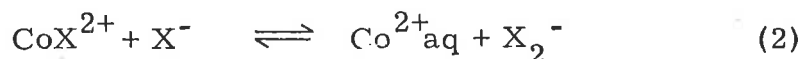
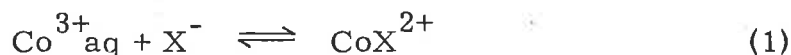
The observation of $\text{CoCl}^{2+}_{\text{aq}}$ rather than $\text{Co}^{3+}_{\text{aq}}$ as the initial product of reaction (4) unequivocally defines the mechanism as inner sphere. As was the case for $\text{Fe}^{2+}_{\text{aq}} + \text{Br}_2^-$ (13.1.3) the rate of reaction of $\text{Co}^{2+}_{\text{aq}}$ with Cl_2^- is very close to that expected for the rate of substitution of Cl_2^- into $\text{Co}^{2+}_{\text{aq}}$. The rate of solvent exchange on $\text{Co}^{2+}_{\text{aq}}$ is $\sim 2 \times 10^6 \text{ s}^{-1}$ (Hunt, 1971). The Eigen-Wilkins mechanism of substitution would predict a rate constant between $\sim 1 \times 10^6$ and $4 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ for substitution of Cl_2^- on $\text{Co}^{2+}_{\text{aq}}$ (K_{IP} between 0.5 and 2 l mol^{-1}). The experimental data are consistent with assignment of mechanism as "inner sphere substitution controlled".

13.2.4 Activation parameters

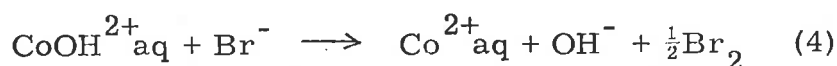
The reaction profile for an inner sphere substitution controlled reaction is shown in Appendix 2.2. The enthalpy of activation for water exchange on $\text{Co}^{2+}_{\text{aq}}$ has been measured by several groups (see Hunt, 1971). The value of 43 kJ mol^{-1} obtained in two different laboratories is probably the most reliable. Our measured activation enthalpy for reaction of Cl_2^- with $\text{Co}^{2+}_{\text{aq}}$ is 9 kJ mol^{-1} less than that for water exchange. As in the case of $\text{Fe}^{2+}_{\text{aq}}$ reacting with Br_2^- and Cl_2^- (inner sphere), where the discrepancies are 10 and 4 kJ mol^{-1} , the difference can be attributed to $\Delta H^{\circ}_{\text{IP}}$. The measured activation parameters are consistent with assignment of the mechanism as "inner sphere substitution controlled".

13.2.5 Literature Comparisons

The hexaaquocobalt (III) ion oxidises bromide and chloride and, more rapidly, iodide ion. For Cl^- and Br^- the reaction is proposed to be inner sphere (Davies and Watkins, 1970).



The intermediate CoCl^{2+} is observed in the reaction of Co^{3+}aq with Cl^- (McAuley et al, 1970). It is apparent that CoCl^{2+} is formed faster than it is removed, i. e. the reaction is "innersphere electron transfer controlled". No intermediate is observed in the Co^{3+}aq , Br^- reaction and it is suggested by Davies and Watkins (1970) that the reaction is limited by the rate of substitution on $\text{CoOH}^{2+}\text{aq}$ ($k_4 \sim 40 \text{ l mol}^{-1} \text{ s}^{-1}$)



In their study of the rate of reduction of Co^{3+}aq , by Cl^- , Sramkova, Zyka and Dolezal (1971) found that the overall rate constant was $1.3 \text{ l mol}^{-1} \text{ s}^{-1}$ at 25°C and $[\text{H}^+] = 1.0 \text{ mol l}^{-1}$. They found that addition of Co^{2+}aq inhibited the reaction and proposed that formation of chlorocobalt (II) complexes bound the available chloride and reduced the observed rate



The limit to the retardation is observed at $[\text{Co}^{2+}\text{aq}] \approx 10^{-2} \text{ mol l}^{-1}$. Current estimates of K_5 suggest a value of $\sim 0.3 \text{ l mol}^{-1}$ (Sillen and Martell, 1969). A value of at least 10^2 l mol^{-1} that would be required to significantly affect $[\text{Cl}^-]$ at $[\text{Co}^{2+}\text{aq}]$ of $10^{-2} \text{ mol l}^{-1}$ seems quite unreasonable. A full kinetic analysis suggests that the retardation is due to reaction of Co^{2+}aq with Cl_2^- (-2) and at sufficiently high $[\text{Co}^{2+}\text{aq}]$ reaction (3) can become rate limiting.

Although the measured rate constant for Co(III) reduction cannot be simply identified with that for reaction (2), the rate of this reaction must be within a factor of 10 of $1.3 \text{ l mol}^{-1} \text{ s}^{-1}$ to account for the observed second order chloride dependence. We can therefore estimate K_2 from this assumed value of k_2 and our value of k_{-2} and using the measured E^0 of the $\text{Co}^{3+}\text{aq}/\text{Co}^{2+}\text{aq}$ couple (Johnson and Sharpe, 1964) can calculate the E^0 of the $\text{Cl}_2^-/\text{Cl}^-$ couple. The standard reduction potential calculated in this way is

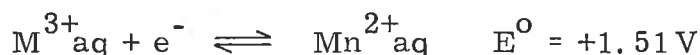


in excellent agreement with the value of 2.29V calculated from thermodynamic data (see Table 11.6A).

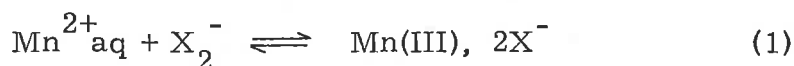
The reactions of halogen radical anions with some low spin Co (II) complexes have been studied by Malone and Endicott (1972). These reactions which bear little relation to oxidation of high spin $\text{Co}^{2+}_{\text{aq}}$ by halogen radical anions have been discussed in detail in 11.6 where it was decided that an inner sphere mechanism was the most likely path of these reactions.

13.3 MANGANESE (II)

In acidic aqueous perchlate media the potential of the Mn(III), Mn(II), half cell is 1.51V. (Davies, 1969)



The free energy changes for reactions of X_2^- with Mn(II)



can be calculated from the estimated X_2^-/X^- couples (see Table 11.6A)



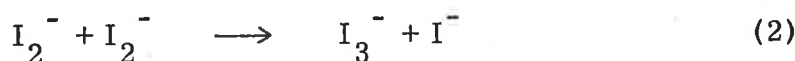
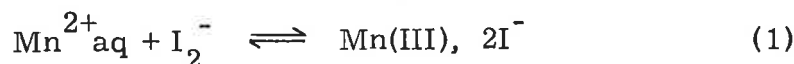
The reactions of Br_2^- and Cl_2^- have negative free energy changes and equilibrium (1) will lie to the right.

Manganese (II) does not react with halogens or hydrogen peroxide and either of the systems X_2/X^- or $\text{H}_2\text{O}_2/\text{X}^-$ can be used to generate X_2^- in the presence of $\text{Mn}^{2+}_{\text{aq}}$.

13.3.1 $\text{Mn}^{2+}_{\text{aq}} + \text{I}_2^-$

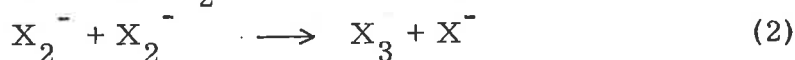
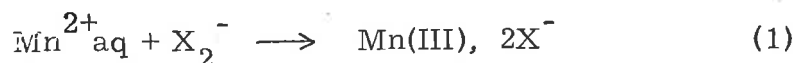
No reaction of $\text{Mn}^{2+}_{\text{aq}}$ with I_2^- could be observed in competition ^{it} with the disproportionation reaction (2). This may be because $k_1 <$

$2 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ and/or the equilibrium constant K_1 is much less than unity.



13.3.2 Rates and temperature dependence $\text{Mn}^{2+}_{\text{aq}} + \text{X}_2^-$

In the presence of $\text{Mn}^{2+}_{\text{aq}}$ (10^{-3} - $2 \times 10^{-2} \text{ mol l}^{-1}$) the rate of decay of Br_2^- and Cl_2^- from halogen solutions was significantly increased. The decay was analyzed in terms of competing second order disproportionation and pseudo first order reactions. The pseudo first order rate constant was approximately linearly dependent on $[\text{Mn}^{2+}_{\text{aq}}]$ at low $[\text{Mn}^{2+}_{\text{aq}}]$ but tended to become $[\text{Mn}^{2+}_{\text{aq}}]$ independent at high $[\text{Mn}^{2+}_{\text{aq}}]$.



Plots of k_1 the pseudo first order rate constant against $[\text{Mn}^{2+}_{\text{aq}}]$ are shown at a variety of temperatures in figures 13.3A and 13.3B. Analysis of the $[\text{Mn}^{2+}_{\text{aq}}]$ dependence and temperature dependence of the rate constants is covered in 13.3.3 and 13.3.5.

13.3.3 $\text{Mn}^{2+}_{\text{aq}}$ dependence

Investigation of possible artifacts, such as limitations caused by the response time of the apparatus, in the measurement of the pseudo first order rate constant proved that the tendency toward $[\text{Mn}^{2+}_{\text{aq}}]$ independence at high $[\text{Mn}^{2+}_{\text{aq}}]$ was a real chemical effect.

For a reaction between oppositely charged ions $\text{Mn}^{2+}_{\text{aq}}$ and X_2^- a fall in the rate constant with increasing ionic strength is expected, but in the experiments the ionic strength increased only from 0.20 to 0.26 mol l^{-1} over the range of $\text{Mn}^{2+}_{\text{aq}}$ concentrations. The rate constant for reaction of Cl_2^- with $\text{Mn}^{2+}_{\text{aq}}$ was found to be independent of ionic strength in this range.

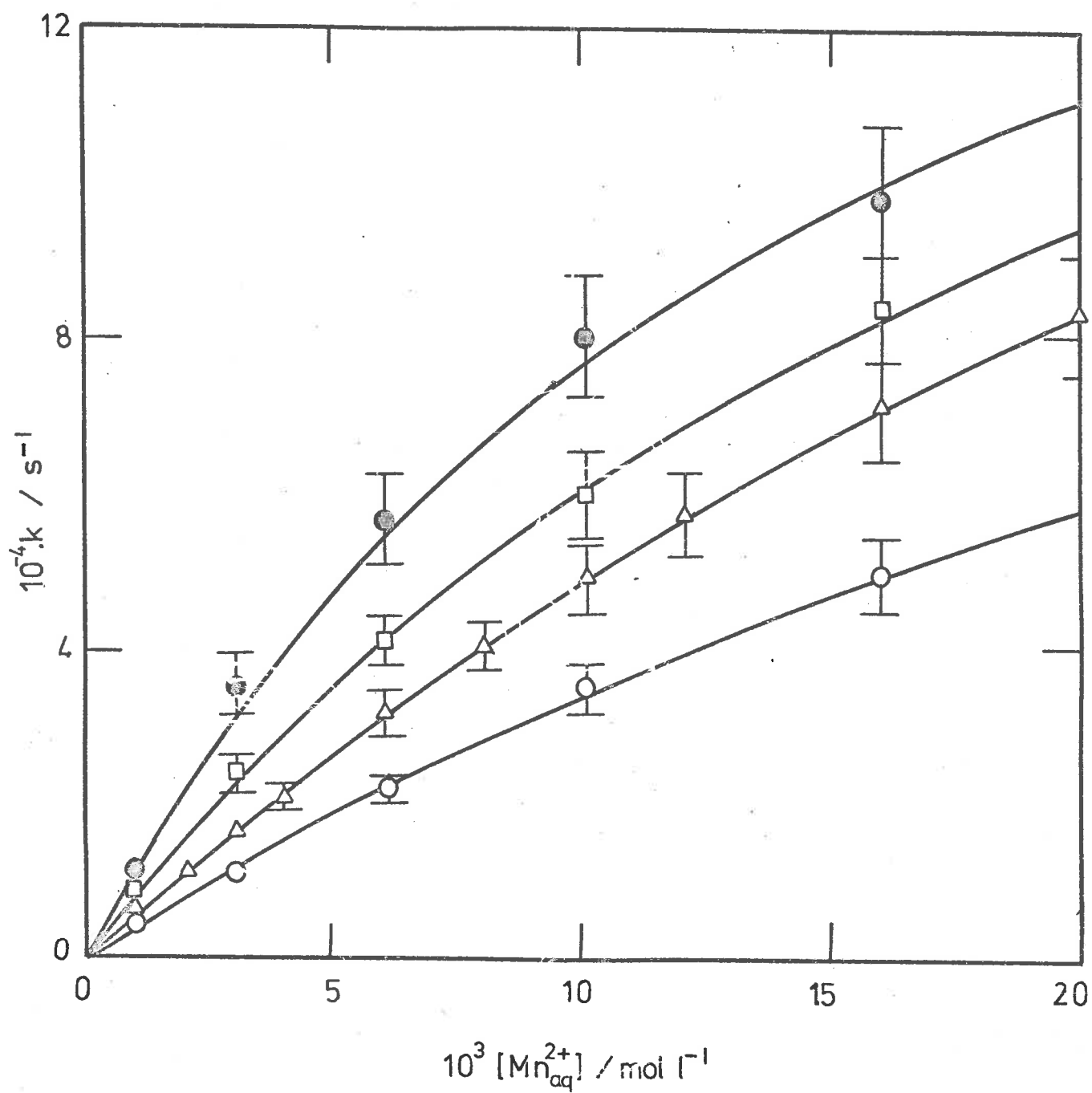


Fig. 13.3A $\text{Mn}^{2+}_{\text{aq}} + \text{Br}_2$, Dependence of Pseudo First Order Rate Constant on $[\text{Mn}^{2+}_{\text{aq}}]$.

(O , 15°C ; Δ , 25°C ; $\square$, 31°C ; $\bullet$, 40°C)

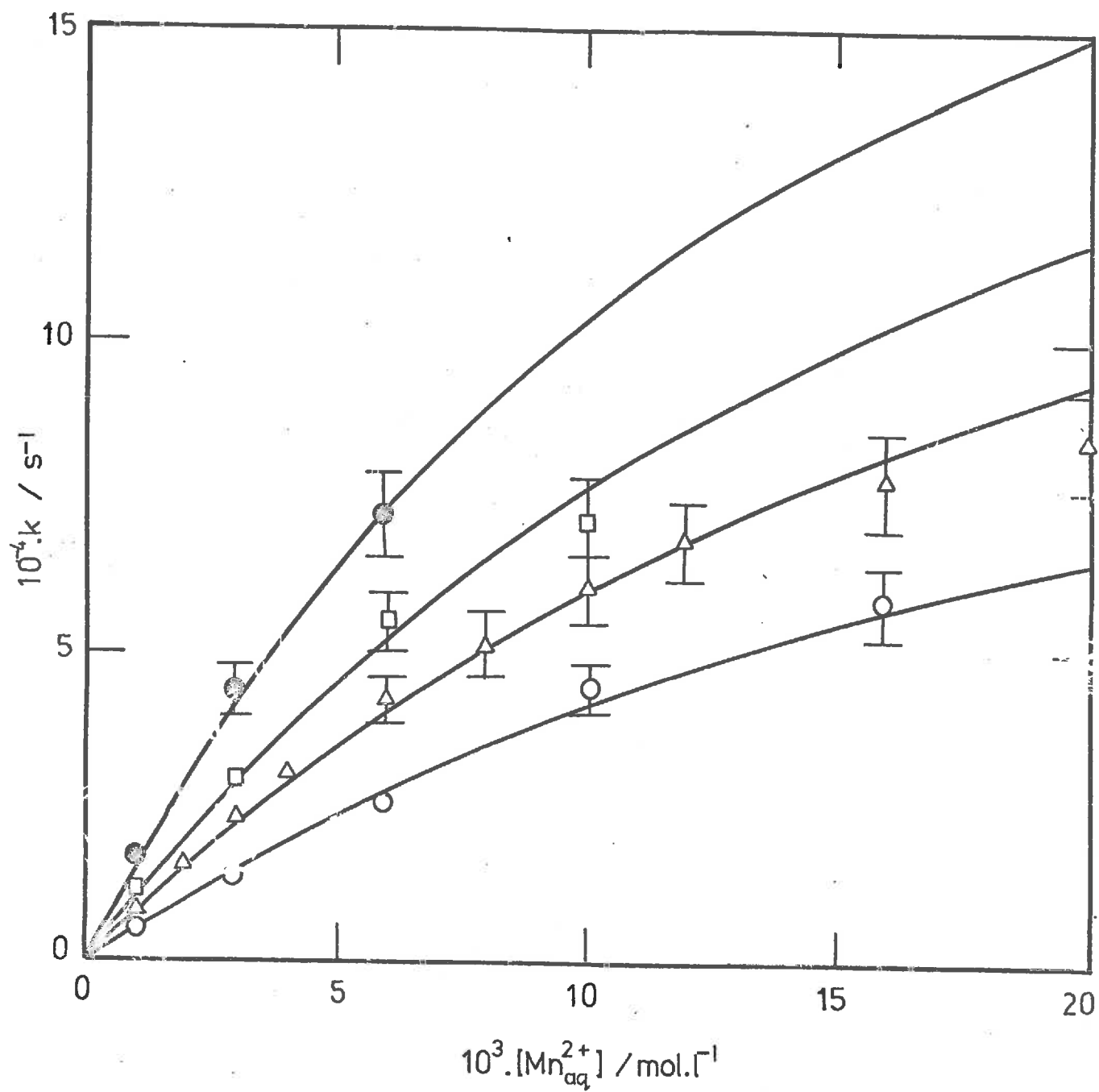
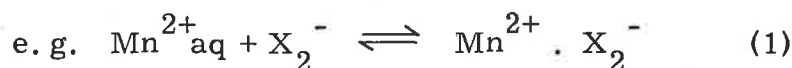


Fig. 13.33 $\text{Mn}^{2+}_{\text{aq}} + \text{Cl}_2$, Dependence of Pseudo First Order Rate Constant on $[\text{Mn}^{2+}_{\text{aq}}]$.
 (○, 16°C; Δ, 25°C; □, 31°C; ●, 40°C.)

The curvature of the plots of pseudo first order rate constant against $[\text{Mn}^{2+}_{\text{aq}}]$ is most simply interpreted in terms of a rapid pre-equilibrium involving $\text{Mn}^{2+}_{\text{aq}}$ and X_2^-



followed by the rate determining step which leads to products either directly or by subsequent fast steps.



If equilibrium (1) is maintained during the reaction the rate of disappearance of X_2^- is

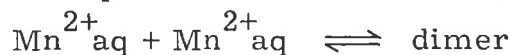
$$-\frac{d[\text{X}_2^-]}{dt} = \frac{k_2 K_1 [\text{X}_2^-] [\text{Mn}^{2+}_{\text{aq}}]}{1 + K_1 [\text{Mn}^{2+}_{\text{aq}}]}$$

In our experiments where $[\text{Mn}^{2+}_{\text{aq}}] \gg [\text{X}_2^-]$, the observed pseudo first order rate constant k is

$$k = \frac{k_2 K_1 [\text{Mn}^{2+}_{\text{aq}}]}{1 + K_1 [\text{Mn}^{2+}_{\text{aq}}]}$$

Rearranging this relationship, $1/k$ should be a linear function of $1/[\text{Mn}^{2+}_{\text{aq}}]$ with intercept $1/k_2$ and slope $1/k_2 K_1$. The reciprocal plots of the experimental data are shown for Br_2^- in Fig. 13.3C and for Cl_2^- in Fig. 13.3D. The expected linear relationship apparently holds over the range of $\text{Mn}^{2+}_{\text{aq}}$ concentrations studied. The values of K_1 , k_2 , and $k_2 K_1$, for Br_2^- and Cl_2^- are shown in Table 13.3A.

[†] Footnote: Other equilibria such as,



could explain the $\text{Mn}^{2+}_{\text{aq}}$ dependence but there is no evidence for significant complexation or dimerization in halide or perchlorate media. $\text{Mn}^{2+}_{\text{aq}}$ is a typical divalent aquo cation (Libus and Sadowska, 1969).

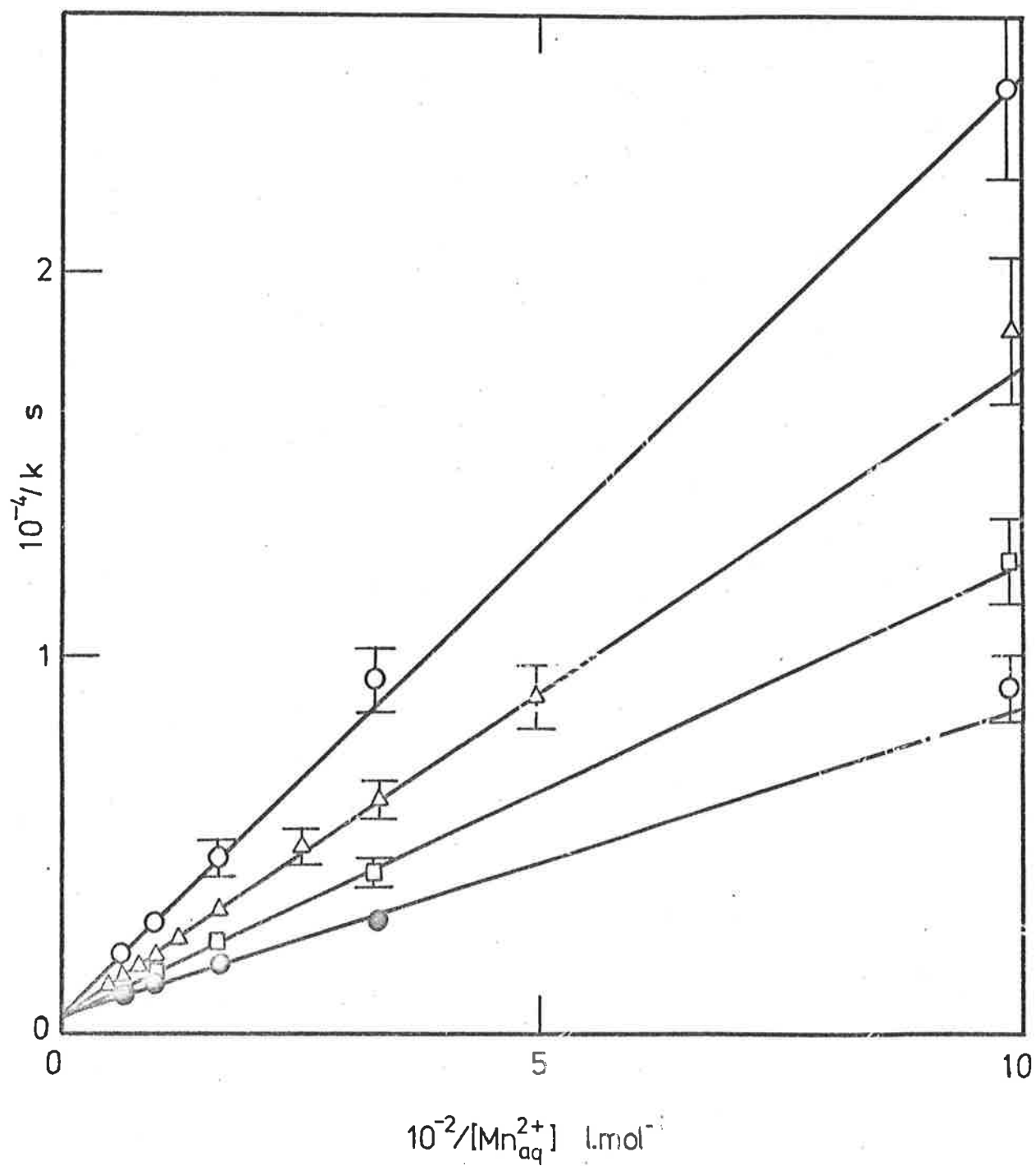


Fig. 13.3C $Mn^{2+}_{aq} + Br_2$, Reciprocal Plot.

(○ , 16°C ; △ , 25°C ; □ , 31°C ; ● , 40°C)

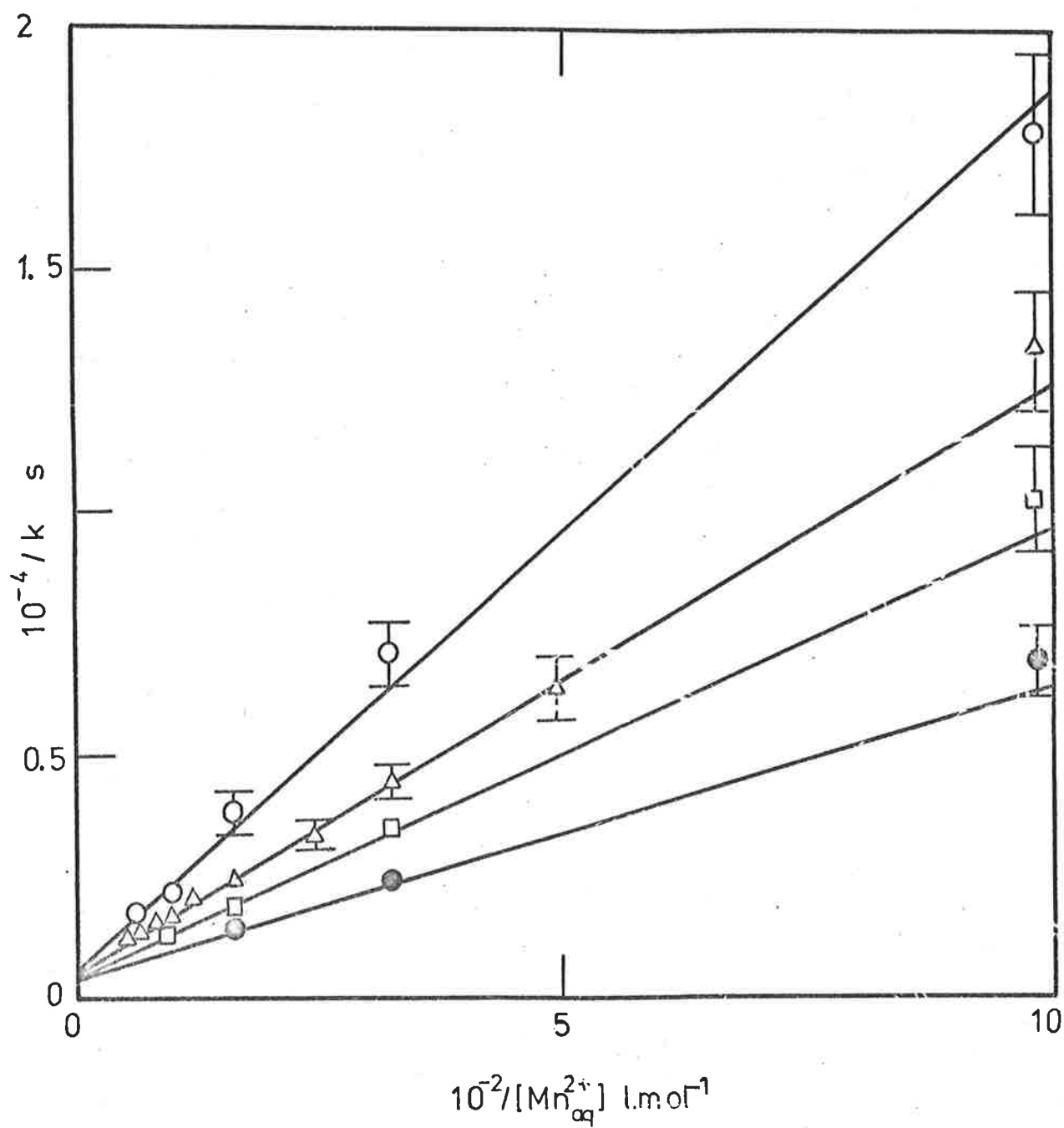


Fig. 13.3D $\text{Mn}^{2+}_{\text{aq}} + \text{Cl}_2$, Reciprocal Plot.
 ($\circ$, 16°C ; Δ , 25°C ; $\square$, 31°C ; $\bullet$, 40°C)

Table 13.3A

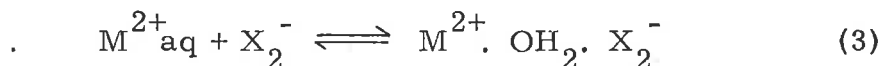
Rate data: $\text{Mn}^{2+}_{\text{aq}} + \text{X}_2^-$

X		16°C	25°C	31°C	40°C	$\Delta H^\ddagger$ kJ mol ⁻¹	$\Delta S^\ddagger$ J mol ⁻¹ K ⁻¹
Br	$K_1 k_2 \times 10^{-6}$ (l mol ⁻¹ s ⁻¹)	4.1 (+ 0.2)	6.0 (+ 0.3)	8.4 (+ 0.5)	12.0 (+ 1.0)	33.6 (+ 4)	-3 (+ 12)
	$k_2 \times 10^{-5}$ (s ⁻¹)	2.1 (+ 0.7)	2.2 (+ 0.7)	3.0 (+ 0.7)	2.2 (+ 0.7)	-	-
	K_1 (l mol ⁻¹)	20 (+ 10)	27 (+ 10)	28 (+ 15)	55 (+ 20)	-	-
Cl	$K_1 k_2 \times 10^{-6}$ (l mol ⁻¹ s ⁻¹)	5.6 (+ 0.3)	8.3 (+ 0.4)	10.8 (+ 1.0)	17.0 (+ 2.0)	32.0 (+ 4)	-4 (+ 12)
	$k_2 \times 10^{-5}$ (s ⁻¹)	1.6 (+ 0.6)	2.1 (+ 0.6)	2.5 (+ 0.6)	2.7 (+ 0.7)	-	-
	K_1 (l mol ⁻¹)	35 (+ 15)	40 (+ 15)	43 (+ 20)	63 (+ 20)	-	-

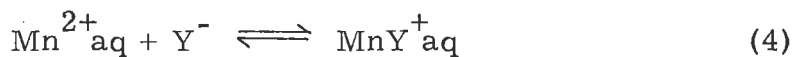
The errors in the values of K_1 and k_2 are larger than the error in the product $K_1 k_2$ and although the observed temperature dependence of $K_1 k_2$ cannot sensibly be split into an enthalpy term for K_1 and an enthalpy of activation for k_2 , the observed enthalpy and entropy parameters for $K_1 k_2$ can be calculated with more certainty. (See Table 13.3A)

From the derived values of K_1 and k_2 the dependence of the pseudo first order rate constant on $[\text{Mn}^{2+}_{\text{aq}}]$ can be calculated. The solid lines in Figures 13.3A and 13.3B are the computed dependencies using values in Table 13.3A. The observed fit of the experimental data is excellent. The chosen reaction scheme appears to adequately represent the events occurring.

From the magnitudes of K_1 some inference on the nature of the $\text{Mn}^{2+} \cdot \text{X}_2^-$ adduct can be made. An outer sphere complex or ion pair is unlikely to show a stability constant (K_1) of 40 l mol^{-1} . From the Fuoss relationship (1958) and absolute upper limit of 10 l mol^{-1} can be estimated. Kinetic measurements on the $\text{Fe}^{2+}_{\text{aq}}$, X_2^- and $\text{Co}^{2+}_{\text{aq}}$, Cl_2^- reactions give values of $\sim 1.5 \text{ l mol}^{-1}$ (See 13.1.2, 13.2.3)



Inner sphere complexes or manganese (II) with various anions have been observed and their stability constants (K_4) evaluated (Sillen and Martell, 1969).



Equilibrium constants from 1 to 10 l mol^{-1} have been measured for halide ions. Thiocyanate shows an equilibrium constant of 17 l mol^{-1} . A value of 40 l mol^{-1} is higher than any stability constant yet measured for a Mn (II) complex with a uninegative anion, but may arise from the polarizability of the large X_2^- ligand.

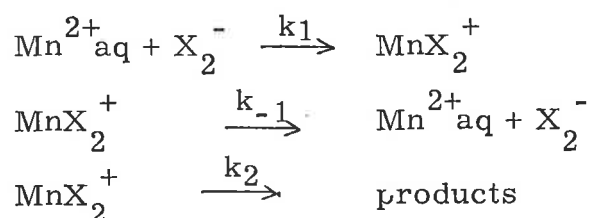
If the complex is an inner sphere $\text{Mn}^{\text{II}}\text{X}_2^+$ complex, substitution rates on $\text{Mn}^{2+}_{\text{aq}}$ can be used to estimate more parameters of the system.

The best estimate of the rate of loss of water from the first coordination sphere of $\text{Mn}^{2+}_{\text{aq}}$ (solvent exchange) is $2.3 \times 10^7 \text{ s}^{-1}$ (Swift and Connick, 1962; Grant, Dodgen and Hunt, 1971). The rate of formation of $\text{MnCl}^+_{\text{aq}}$ (i. e. substitution of Cl^- ; k_5) has been measured as $1.5 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ (Hayes and Myers, 1964).



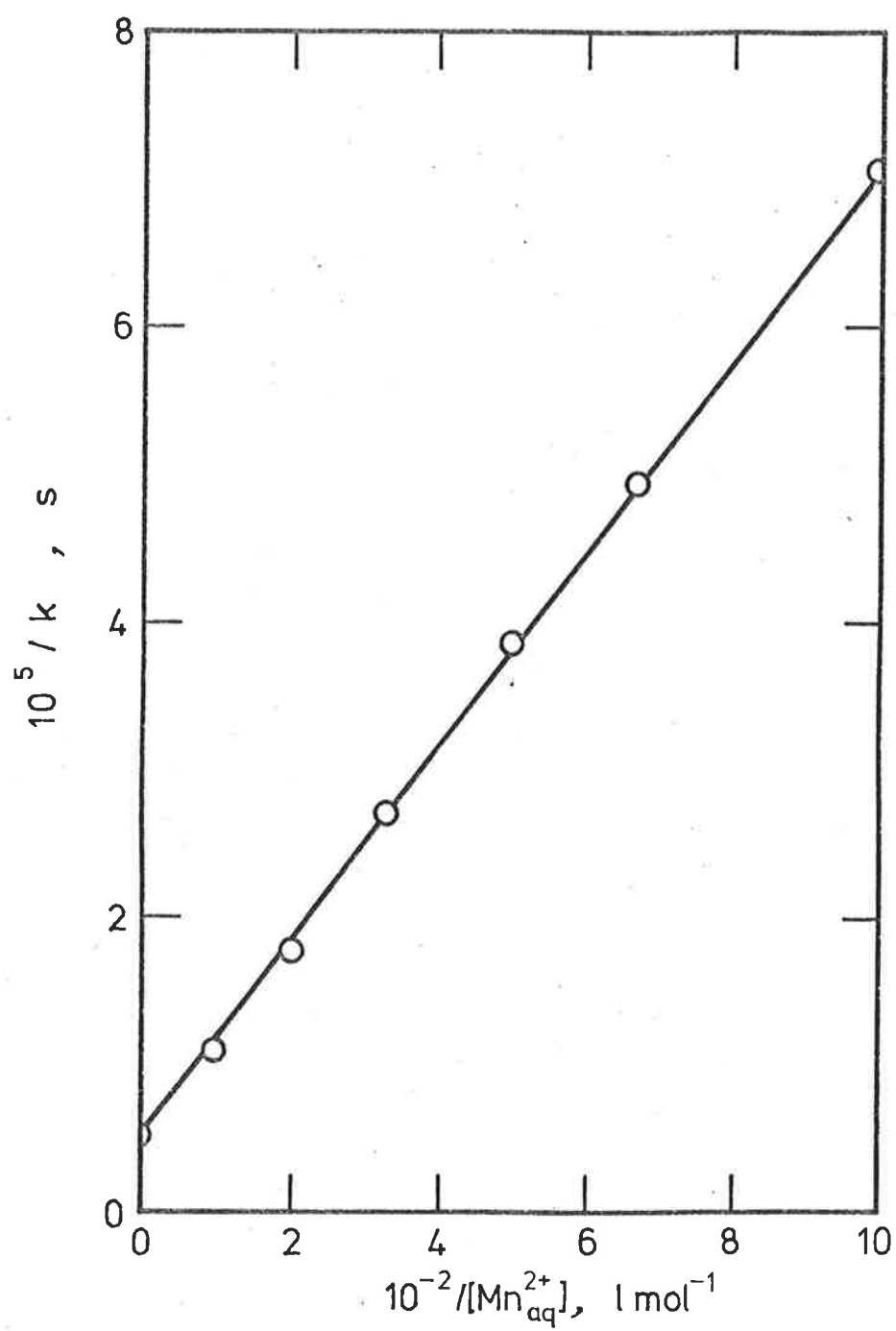
The value of k_1 for substitution of X_2^- is almost certainly within a factor of 2 of $2 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$. From $K_1 \approx 40 \text{ l mol}^{-1}$, k_{-1} can be calculated as $\sim 5 \times 10^5 \text{ s}^{-1}$. It is clear that the assumption $k_{-1} \gg k_2$, necessary for the maintenance of equilibrium (1) does not strictly hold (cf $k_2 \approx 2 \times 10^5 \text{ s}^{-1}$) but without this assumption data treatment is complex.

The validity of the simple data treatment has been investigated using computer simulation studies (See 3.4.3). For an initial X_2^- concentration, the X_2^- concentrations in the presence of Mn^{2+} were calculated as a function of time using the rigorous scheme below (Program WR16 - See appendix 1.4).



The decay of X_2^- was first order and the pseudo first order rate constant showed a similar $[\text{Mn}^{2+}_{\text{aq}}]$ dependence to the experimental results. When treated as a reciprocal plot ($1/k$ against $1/[\text{Mn}^{2+}_{\text{aq}}]$) the simulated data did not fit a perfect straight line, as would be expected if the assumption of fast pre-equilibrium was valid. A typical reciprocal plot of the data from a simulation experiment is shown in Fig. 13.3E. The deviations from linearity are within experimental error over the covered range. From the best fit slope and intercept of the simulated reciprocal plot, values of " K_1 " and " k_2 " can be

Fig. 13.3E $\text{Mn}^{2+} + \text{X}_2^-$: Simulated Reciprocal Plot



calculated. The intercept gives a value of " k_2 " which is slightly dependent upon the range of $[Mn^{2+}_{aq}]$ covered but always within experimental error of the true value of k_2 chosen for the simulation. The measured value of " K_1 "[†] is however, significantly smaller than the chosen value of K_1 given by k_1/k_{-1} (In the example given in Fig. 13.3E for $k_1 = 2 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, $k_{-1} = 4 \times 10^5 \text{ s}^{-1}$, $k_2 = 2 \times 10^5 \text{ s}^{-1}$; " K_1 " observed = 33 l mol^{-1} cf K_1 true 50 l mol^{-1}). Over a wide range of $[Mn^{2+}_{aq}]$ and chosen values of k , k_{-1} and k_2 the empirical relationship (6) was observed.

$$"K_1" \text{ obs} = \frac{k_1}{k_{-1} + k_2} \quad (6)$$

Assuming a value of $k_1 = 2 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$, from " K_1 " obs and k_2 a value of the true equilibrium constant $K_1 (= k_1/k_{-1})$ can be calculated. At 25°C the values obtained are:

$$\text{Br}_2^- : K_1 = 39 \pm 15 \text{ l mol}^{-1}$$

$$\text{Cl}_2^- : K_1 = 68 \pm 30 \text{ l mol}^{-1}$$

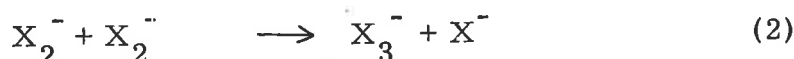
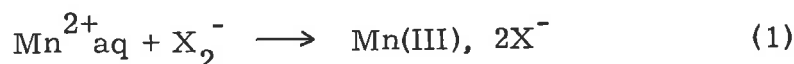
These values are higher than those calculated from the experimental reciprocal plots but arguments about the nature of the MnX_2^+ complex are not affected by this revision of values.

This specific example has relevance to the general application of the widely invoked assumption of rapid pre-equilibrium. It is apparent that unless the value of the equilibrium back reaction is at least five times faster than the subsequent rate determining step, the values of the pre-equilibrium constant and the subsequent rate constant cannot be evaluated (within $\sim 5\%$) by the assumption of rapid equilibrium.

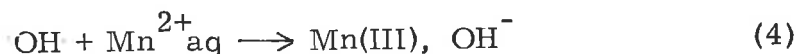
[†] Footnote: " K_1 " will only be k_1/k_{-1} if the assumption of fast pre-equilibrium holds.

13.3.4 Mechanism

After the disappearance of X_2^- in a solution containing sufficient Mn^{2+}_{aq} to compete efficiently with the disproportionation reaction (2)



a semi permanent ($t_{1/2} \sim \text{min}$) absorbance in the 300 - 500 nm region was observed. The spectra of these products are shown in Fig. 13.3F and compared with a normalized spectrum of $Mn(III)_{aq}$ (Diebler & Sutin, 1964). A solution of hydrogen peroxide and acid containing Mn^{2+}_{aq} but no halide ion produced a similar transient when flashed. The spectrum of this transient (which is presumably formed from reaction of hydroxyl radicals with Mn^{2+}_{aq} (Brown, Dainton, Walker & Keene, 1965)) is also shown in Fig. 13.3F.

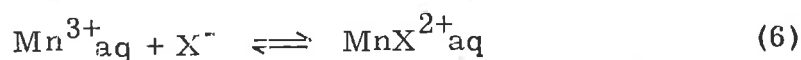


The observed spectra are identical and, based on a 1:1 stoichiometry with X_2^- yield, show the same extinction coefficient at 470 nm ($\epsilon = 150 \pm 50$). The spectrum of $Mn(III)_{aq}$, under the same conditions is, within the limits of experimental error, the same as the observed spectra.

The hydrolysis constant, K_5 , of Mn^{3+}_{aq} is 0.93 (Wells & Davies, 1967)



and the formation constants, K_6 , of monohalogeno complexes around 10 l mol^{-1} (Davies, 1969)



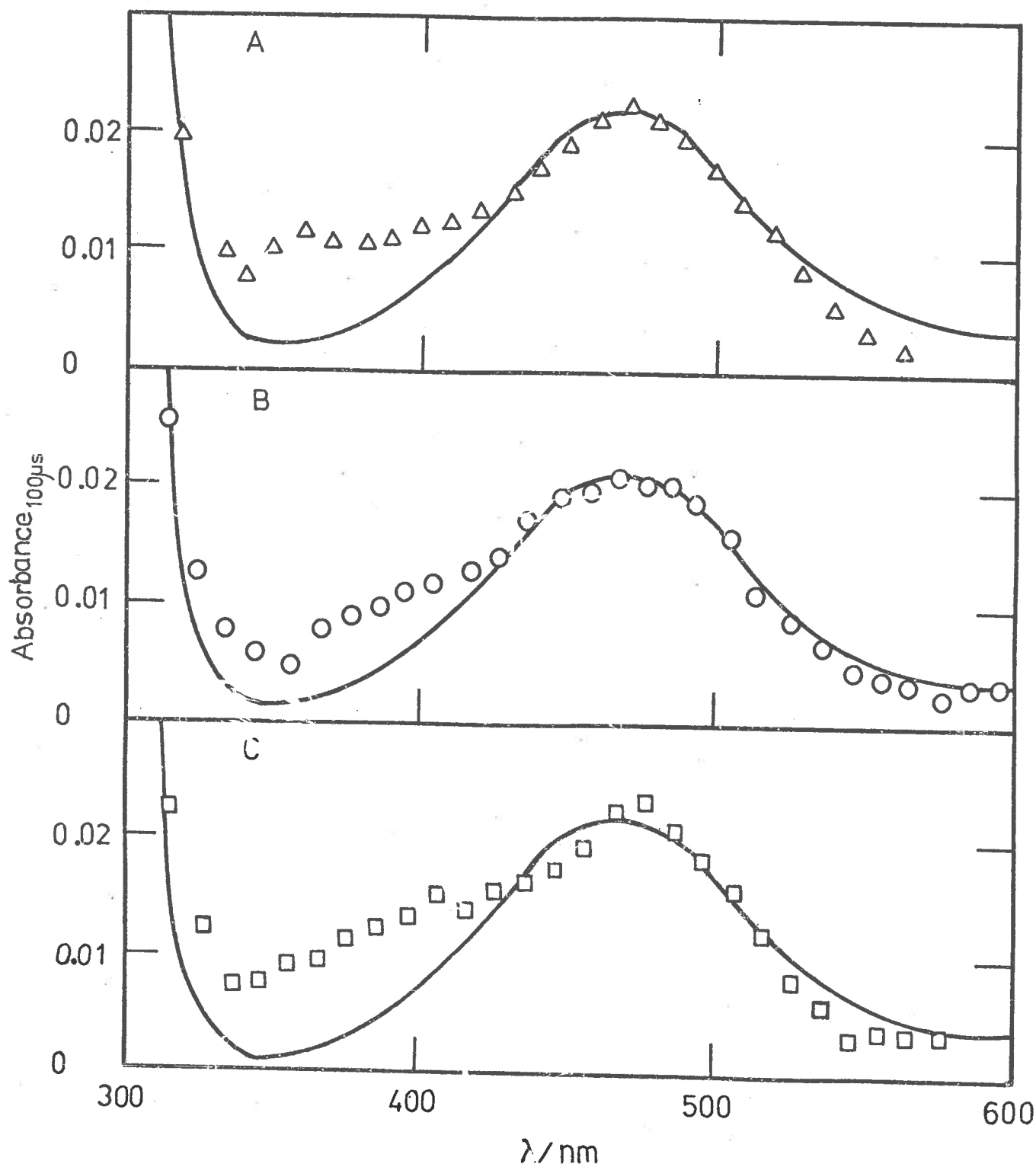


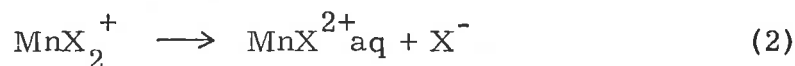
Fig. 13.3F Transient Spectra, $\text{Mn}^{2+}_{\text{aq}} + \text{Br}_2^-$ (Δ), $+ \text{OH}^-$ ($\circ$), $+ \text{Cl}_2^-$ ($\square$)
Reported Spectrum of $\text{Mn}^{3+}_{\text{aq}}$ (—).

In our solutions ($10^{-1} \text{ mol l}^{-1} \text{X}^{-}$, $10^{-1} \text{ mol l}^{-1} \text{H}^{+}$) the equilibrium ratio of Mn (III) products would be 90% $\text{MnOH}^{2+}_{\text{aq}}$, 5% $\text{Mn}^{3+}_{\text{aq}}$, 5% $\text{MnX}^{2+}_{\text{aq}}$. The observed spectra are in agreement with this prediction (i. e. the manganese (III) product is equilibrated within 100 μsec). Although Mn(III) is labile neither the rate of solvent exchange or ligand substitution have been measured. Assuming that the fastest measured Mn(III) oxidations are controlled by the rate of loss of solvent (i. e. are inner sphere substitution controlled) Davies (1969) estimated the rate of solvent exchange on $\text{MnOH}^{2+}_{\text{aq}}$ to be $\sim 10^6 \text{ s}^{-1}$. If this figure is correct the initial Mn(III) product will equilibrate well within the minimum observation time of our apparatus.

Product observation in this system is of no use in determining mechanism. The initial Mn(III) product ($\text{Mn}^{3+}_{\text{aq}}$ or $\text{MnX}^{2+}_{\text{aq}}$) is too labile to observe. The mechanism may however be inferred from kinetic evidence. The $[\text{Mn}^{2+}_{\text{aq}}]$ dependence of the rate constant has been explained in terms of precursor complex formation. This complex shows a large stability constant and is an inner sphere rather than ion-pair complex. The kinetic inference of an inner sphere intermediate is conclusive evidence that the reaction is inner sphere. The rate constant of the subsequent electron transfer step is rate limiting and is obviously less than the substitution rate, hence the reaction is electron transfer controlled (See 11.4.2, 11.3).

13.3.5 Activation parameters

The enthalpy and entropy of activation of the function Kobs . $k_2 = \frac{k_1 k_2}{k_{-1} + k_2}$ (see 13.3.3) have been determined.



These terms cannot sensibly be related to individual steps in the mechanism. For an inner sphere electron transfer controlled

mechanism the activation enthalpy for electron transfer must be larger than the activation enthalpy of substitution (See Appendix 2.1). The observed over all activation enthalpies (34 ± 4 and 32 ± 4 kJ mol⁻¹ for Br₂⁻ and Cl₂⁻ respectively) are approximately equal to the activation enthalpies of substitution of Cl⁻ on Mn²⁺aq (39 ± 4 kJ mol⁻¹; Hayes & Myers, 1964) and water exchange on Mn²⁺aq (36 ± 4 kJ mol⁻¹; Grant, Dodgen and Hunt, 1971) and significantly larger than any of the activation enthalpies previously measured (See 13.1.5, 13.2.4), despite the more favourable free energy change for Mn²⁺aq + Cl₂⁻ than for Co²⁺aq + Cl₂⁻.

For inner sphere substitution controlled reactions of Fe²⁺aq and Co²⁺aq with X₂⁻, the observed activation energy barrier, which is essentially that for substitution of X₂⁻ into M²⁺aq, is approximately 3 kJ mol⁻¹ less than the activation energy for water exchange. The lower value has been attributed to the enthalpy of formation of the ion pair (see 13.1.5), which would also be operative in the case of Mn²⁺aq. The height of the barrier for substitution on Mn²⁺aq can be estimated as the enthalpy of activation for water exchange (36 ± 4 kJ mol⁻¹) plus the enthalpy of formation of the outer sphere complex or ion pair (-8 kJ mol⁻¹) i. e. ~ 28 kJ mol⁻¹. The observed activation energies for the Mn²⁺aq, X₂⁻ reactions are significantly larger than this value supporting the conclusion that the reaction rate is controlled by the height of the barrier to electron transfer rather than that for substitution.

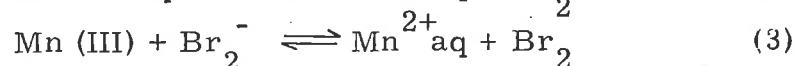
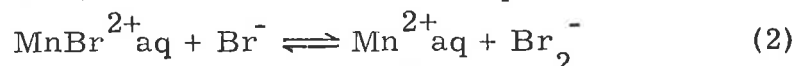
13.3.6 Effect of varying X₂⁻

The measured rate and activation parameters for the Mn²⁺aq, Cl₂⁻ and Mn²⁺aq, Br₂⁻ systems are, despite the difference of 50 kJ mol⁻¹ in overall free energy change, identical within the limits of experimental error. This observation is somewhat unexpected for an electron transfer controlled reaction where the same sort of linear free energy relationship as for an outer sphere reaction (i. e. the larger the free energy

change the smaller the barrier) might be expected. Additionally the reaction of Co^{2+}aq with Cl_2^- has a free energy change approximately intermediate between Mn^{2+}aq , Br_2^- and Mn^{2+}aq , Cl_2^- and yet is not limited by the rate of electron transfer. These observations can only be rationalized if the barrier to electron transfer in the $\text{Mn}^{\text{II}}\text{X}_2^+$ complex is largely due to a specific energetic requirement imposed by the central cation and is little influenced by the magnitude of the overall free energy change. The possibility of such a requirement is discussed in 13.9.

13.3.7 Literature comparisons

Reactions of manganese (II) with halogen radical anions have been proposed in studies of the catalysis of the halogen, oxalic acid (Taube, 1947, 1948) and halogen, hydrogen peroxide (Morrow and Silver, 1972; Davies and Kustin 1973) reactions by the manganese(II) manganese(III) couple and in studies of the photochemical dissociation of halogens and trihalide ions using Mn^{2+}aq as a radical scavenger (Rutenberg and Taube, 1950, 1951). No observations on the nature or rate of the proposed reactions were made. Wells and Mays (1968) studied the reaction of Mn(III) and Br^- in the presence of Mn^{2+}aq . The proposed mechanism was,



The present results show indirectly that the reaction between Mn^{2+}aq and Br_2^- (-2) does produce the inner sphere $\text{MnBr}^{2+}\text{aq}$ product. From the observations of Wells and Mays (1968) on the value of k_2 and our value of k_{-2} a value of K_2 can be calculated and hence the E° for the $\text{Br}_2^-/\text{Br}^-$ couple. From Wells and Mays data the product $K_1 k_2$ is $3.6 \times 10^5 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ and consequently $K_1 K_2$ is $6 \times 10^{-2} \text{ l mol}^{-1}$ and

the E^0 for the $\text{Br}_2^-/\text{Br}^-$ couple is +1.62 V. In view of the different conditions under which k_2 and k_{-2} were measured, particularly ionic strength, the agreement with our value of +1.77 V is satisfactory.

Wells and Mays discounted the importance of k_{-2} in their experiments because they found no $[\text{Mn}^{2+}_{\text{aq}}]$ retardation which could be attributed to this reaction. They assumed $k_3 > k_{-2}$ which in view of the value of k_{-2} we have measured directly ($\sim 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$) maybe an unreasonable assumption. The lowest $\text{Mn}^{2+}_{\text{aq}}$ concentration in the work of Wells and Mays was 0.3 mol l^{-1} . From our value of the equilibrium constant for formation of the $\text{Mn}^{\text{II}}\text{Br}_2^+$ complex ($\sim 40 \text{ l mol}^{-1}$) it can be estimated that approximately 92% of Br_2^- is complexed by this $[\text{Mn}^{2+}_{\text{aq}}]$ and consequently increasing the concentration of manganese (II) can only lead to an 8% increase in the amount of Br_2^- complexed or the rate of reaction (-2). A variation of 8% is within the limits of error of the work of Wells and Mays. This observation indirectly supports our observation that the rate becomes independent of $[\text{Mn}^{2+}_{\text{aq}}]$ at high $[\text{Mn}^{2+}_{\text{aq}}]$, i. e. that the reaction is inner sphere electron transfer controlled.

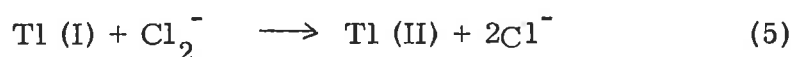
The oxidation of Cl^- by $\text{Mn}^{3+}_{\text{aq}}$ has not been investigated directly. Solutions of $\text{Mn}^{3+}_{\text{aq}}$ containing Cl^- are effectively stable and this is not surprising in view of the unfavourable free energy change of $+83 \text{ kJ mol}^{-1}$ for the reaction.



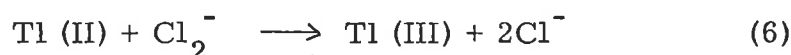
If the reaction is to proceed through this mechanism the minimum activation energy is $+83 \text{ kJ mol}^{-1}$. The reaction has been proposed by Rossiensky and Hill (1972) to account for the chloride ion catalyzed oxidation of Ti^+_{aq} by Mn(III) . They obtained a value of $1.16 \text{ l mol}^{-1} \text{ s}^{-1}$ for k_4 which coupled with our measured value of k_{-4} leads to a value for the standard reduction potential of Cl_2^- of +1.86 V, very much lower than the 2.29 V calculated from thermodynamic data (see

Appendix 2.3) and confirmed by kinetic data for the oxidation of Cl^- . It is probable that the course of the chloride catalyzed reaction between Mn(III) and Tl(I) is more complex than Rossiensky and Hill assumed.

Cl_2^- was proposed as the active oxidant not only of Tl(I)



but also of Tl(II)



Typical concentrations in their system were (Mn(III) , $10^{-3} \text{ mol l}^{-1}$; Mn(II) , 10^{-1} ; Tl(I) , $10^{-2} \text{ mol l}^{-1}$; Cl^- , $10^{-2} \text{ mol l}^{-1}$). The stationary state concentration of Cl_2^- can be calculated from their data and our value of k_{-4} as $10^{-11} \text{ mol l}^{-1}$

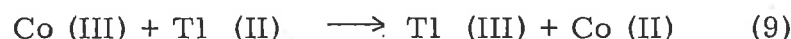


They neglected reactions of Tl(II) with Mn(III) and Mn(II) .



If one assumes as an upper limit that k_6 is diffusion controlled (i. e. $10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$) then given concentrations of Cl_2^- , Mn(III) and Mn(II) we can calculate that if reaction (6) is to predominate, k_7 must be less than $10^2 \text{ l mol}^{-1} \text{ s}^{-1}$ and k_8 less than $1 \text{ l mol}^{-1} \text{ s}^{-1}$.

The rate of reaction (9) has been measured in this laboratory (Falcinella and Laurence; to be published)

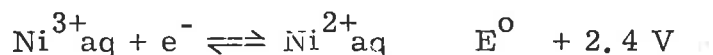


It might be expected that k_9 and k_7 would be of the same order ($\sim 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ for k_9). Falcinella and Laurence have also measured k_8 directly as $1.9 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ at 25°C . It is obvious that reaction (8) and probable that reaction (7) will compete very effectively for Tl(II) . It is apparent that the scheme of Rossiensky and Hill (1972) is a gross

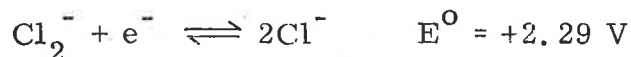
simplification. With the measurement of the Mn(III), Tl(II) rate constant a re-evaluation of their data will be possible.

13.4 NICKEL (II)

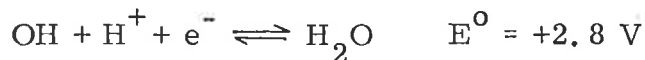
The aquo or hydroxyaquonickel (III) ion has not been detected in solution. With strongly complexing ligands Ni(III) complexes in the solid state have been prepared (Cotton and Wilkinson, 1970) but their solution chemistry is little studied. Meyerstein (1972) has studied the transient produced from hydroxyl radical oxidation of amminenickel (II) complexes and suggests it is an amminenickel (III) complex which decays with a half life of seconds in aqueous solution. The E^0 for the $\text{Ni}^{2+}_{\text{aq}}, \text{Ni}^{3+}_{\text{aq}}$ couple cannot be estimated with any certainty but it is probable that if it were less than 2.4 V $\text{Ni}^{3+}_{\text{aq}}$ would be observable ($\text{Cu}^{3+}_{\text{aq}}$ with an E^0 of +2.4 V is observed, - see 13.5)



It is probable that none of the halogen radical anions are sufficiently strong oxidising agents to oxidise $\text{Ni}^{2+}_{\text{aq}}$. Of the three, Cl_2^- with an E^0 of +2.29 V is most likely to effect the oxidation.



Hydroxyl radicals are powerful oxidising agents. In acidic solution the reduction potential of +2.8 V may be sufficient to oxidise $\text{Ni}^{2+}_{\text{aq}}$.

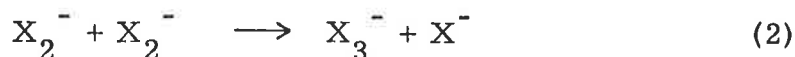
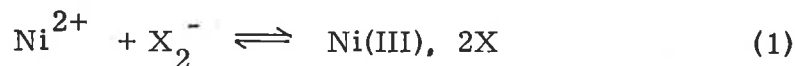


$\text{Ni}^{2+}_{\text{aq}}$ does not react with halogens or hydrogen peroxide and either of these systems is suitable for study of the possible X_2^- or OH reactions.

13.4.1 Br_2^- , I_2^-

A $5 \times 10^{-2} \text{ mol l}^{-1}$ concentration of $\text{Ni}^{2+}_{\text{aq}}$ produces no increase in the rate of decay of Br_2^- or I_2^- from a halogen solution. Reaction (1)

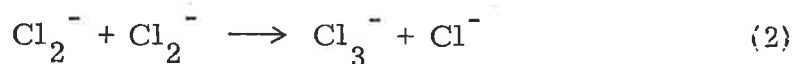
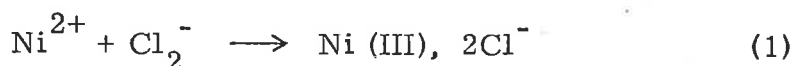
does not compete with the disproportionation reaction (2).



This may be because K_1 is small and/or k_1 is less than $10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

13.4.2 Cl_2^-

In the presence of Ni^{2+} aq decay of Cl_2^- (from Cl_3^- solution) was mixed first and second order. The pseudo first order component was proportional to $[\text{Ni}^{2+} \text{ aq}]$ within the studied range ($10^{-2} - 7 \times 10^{-2} \text{ mol l}^{-1}$)

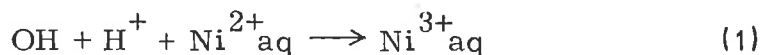


The bimolecular rate constant k_1 can be calculated as $3 \pm 1 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ at $22 \pm 2^\circ \text{C}$.

13.4.3 OH^-

To support the observation of the apparent oxidation of $\text{Ni}^{2+} \text{ aq}$ by Cl_2^- , the previously unreported reaction of $\text{Ni}^{2+} \text{ aq}$ with hydroxyl radicals was studied by pulse radiolysis. No product from reaction of hydroxyl radicals with $\text{Ni}^{2+} \text{ aq}$ could be observed in the region 300 - 1100 nm.

The effect of $\text{Ni}^{2+} \text{ aq}$ on the yield of Cl_2^- from a chloride solution was observed to try and estimate the rate of the $\text{Ni}^{2+}, \text{OH}^-$ reaction by competition. Only a very small effect was observed at very high $\text{Ni}^{2+} \text{ aq}$. The rate of reaction (1) was estimated as $\leq 3 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ in agreement with the observation of Shastri (1969) who found $k_1 \leq 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$.

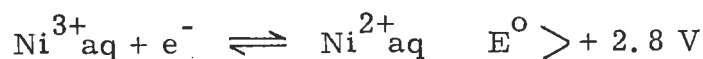


13.4.4 Conclusions

In an attempt to rationalize the above results the purity of the

nickel perchlorate solutions was investigated. The Fluka nickel perchlorate used in the hydroxyl radical reaction studies was ~99% pure but the G. F. Smith nickel perchlorate used in the Cl_2^- reactions was found to contain ~2% cobalt (by atomic absorption spectroscopy). Cl_2^- reacts with Co^{2+}aq at a rate of $1.4 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ (Section 13.2.2) so that a nickel (II) solution containing $2 \pm 0.5\%$ cobalt (II) would exhibit an apparent bimolecular rate constant for reaction with Cl_2^- of $2.8 \pm 0.7 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ if Ni^{2+}aq does not react significantly with Cl_2^- . This value is in excellent agreement with the observed rate constant of $3 \pm 1 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ for the apparent $\text{Ni}^{2+}\text{aq}, \text{Cl}_2^-$ reaction. The rate of any reaction of Ni^{2+}aq with Cl_2^- can be estimated to be less than $10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

It is probable that none of the radical anions, nor hydroxyl radicals react with Ni^{2+}aq . If this is because of unfavourable free energy changes the $\text{Ni}^{2+}\text{aq}, \text{Ni}^{3+}\text{aq}$ couple can be estimated as certainly $> +2.3 \text{ V}$ and probably $> +2.8 \text{ V}$.



13.5 COPPER (II)

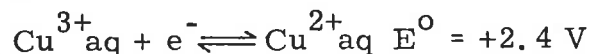
Unlike most other divalent transition metal ions Cu^{2+}aq is more easily reduced than oxidised.



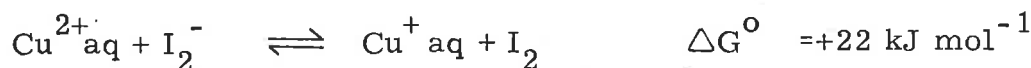
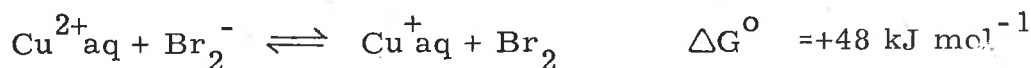
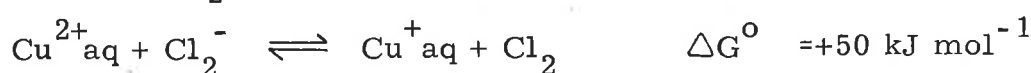
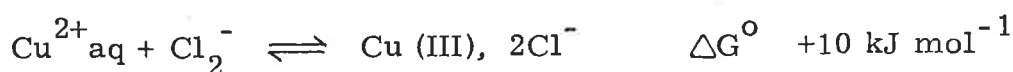
The oxidation of aquo copper (II) ions by hydroxyl radicals has been well documented (Brown, Dainton, Walker & Keene, 1965; Meyerstein, 1971). The rate constant, k_1 , is $3.3 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$.



Meyerstein, (1971) has studied some properties of the aquo and amminecopper (III) complexes and estimated the E^0 for reduction of Cu^{3+}aq as 0.2 V less than that for hydroxyl radicals at pH 3.7. At this pH the standard reduction potential of hydroxyl radicals is 2.6 V.



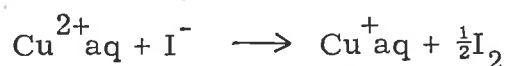
The free energy changes for reduction and oxidation of $\text{Cu}^{2+}_{\text{aq}}$ by X_2^- are listed below. None of the reactions are exothermic according to the estimated potentials.



Copper (II) does not react with halogens or hydrogen peroxide and these systems are suitable for study of the X_2^- reactions, except in the case of I_2^- where the excess iodide necessary to convert I to I_3^- ,



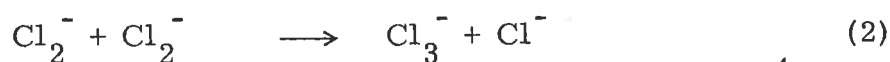
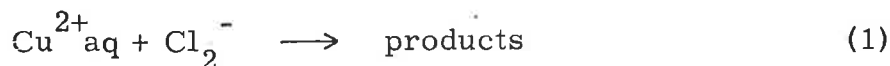
reacts rapidly with $\text{Cu}^{2+}_{\text{aq}}$ (Cotton and Wilkinson, 1967).



Because of this reaction it is impossible to study the reaction of I_2^- with $\text{Cu}^{2+}_{\text{aq}}$ by any method.

13.5.1 Cl_2^-

No reaction of Cl_2^- with $\text{Cu}^{2+}_{\text{aq}}$ was observed in competition with the disproportionation reaction. (2)

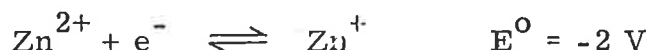


The rate constant k_1 can be estimated as less than $10^4 \text{ l mol}^{-1} \text{ s}^{-1}$. Neither oxidation or reduction of $\text{Cu}^{2+}_{\text{aq}}$ by Cl_2^- takes place with a rate constant in excess of $10^4 \text{ l mol}^{-1} \text{ s}^{-1}$. In view of the unfavourable ΔG° this result is not surprising. The similarity of the free energy

changes for reduction of Cu^{2+}aq by Br_2^- and Cl_2^- suggests that if reaction with Cl_2^- does not occur, reaction with Br_2^- is unlikely.

13.6 ZINC (II)

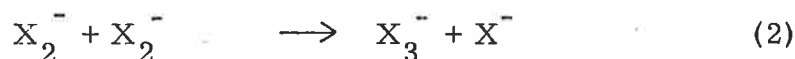
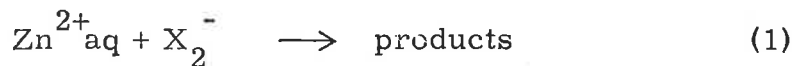
Zn^{2+}aq is relatively inert to redox agents. Oxidation to Zn (III) has not been reported even with strong complexing agents. Reduction of Zn^{2+}aq to Zn^+aq has been accomplished by aquated electrons (Adams, Baxendale & Boag, 1963) but is out of the range of normal reducing agents. The E^0 for the Zn^+aq , Zn^{2+}aq couple has been estimated at -2V (Navon and Meyerstein, 1970)



The halogen radical anions are not sufficiently strong reducing agents to effect this change but in view of the inevitable presence of Zn^{2+}aq in solutions of Fe^{2+}aq , Cr^{2+}aq and V^{2+}aq reduced by zinc amalgam, the effect of Zn^{2+}aq on the rate of decay of Br_2^- and Cl_2^- was investigated. Zinc (II) does not react with halogens or hydrogen peroxide or halide ions. Any of the photochemical systems previously used are suitable for study of the Zn^{2+} , X_2^- reactions.

13.6.1 Cl_2^- , Br_2^-

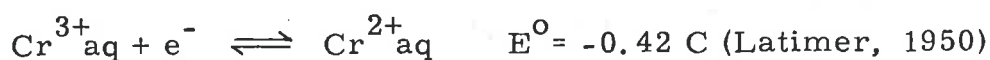
No reaction of zinc (II) with Cl_2^- or Br_2^- could be observed in competition with the disproportionation reaction (2)



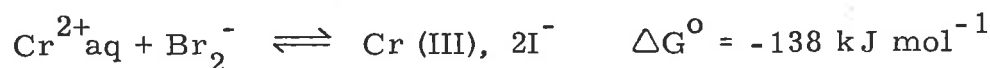
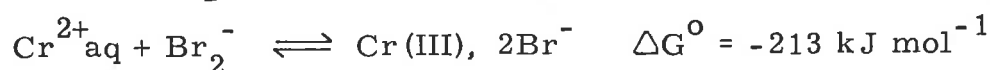
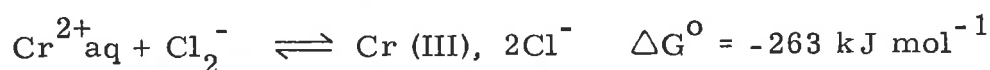
The rate constant, k_1 , can be estimated as less than $10^4 \text{ l mol}^{-1} \text{ s}^{-1}$. It is concluded that the presence of Zn^{2+}aq in solutions of Fe^{2+}aq , Cr^{2+}aq , or V^{2+}aq will not affect the observed rate constants (i. e. zinc amalgam is a suitable reducing agent to prepare the above mentioned solutions).

13.7 CHROMIUM (II)

Chromous ion is a strong reducing agent in aqueous solution.



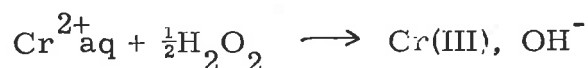
Reaction with all three radical anions is highly exothermic.



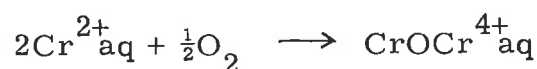
$\text{Cr}^{2+}_{\text{aq}}$ also reacts rapidly with halogens (Taube and Myers, 1954; Ardon and Plane, 1959; Thompson and Gordon, 1966)



with hydrogen peroxide (Samuni, Meisel and Czapski, 1972)



and with oxygen. (Ardon and Plane, 1959)



Armor and Taube (1971) have presented evidence that $\text{Cr}^{2+}_{\text{aq}}$ reacts slowly with N_2O but the rate of the reaction is so slow that in the time scale of our experiments any complication can be neglected.

The only systems suitable for study of X_2^{-} reactions with $\text{Cr}^{2+}_{\text{aq}}$ by flash photolysis or pulse radiolysis are deaerated or nitrous oxide saturated halide solutions.

13.7.1 Preliminary rate measurements

The reliability of techniques for handling $\text{Cr}^{2+}_{\text{aq}}$ in the absence of oxygen restricted the accessible range of $\text{Cr}^{2+}_{\text{aq}}$ concentrations to $>5 \times 10^{-4} \text{ mol l}^{-1}$. Below this concentration, oxidation due to traces of oxygen rendered the concentrations too uncertain.

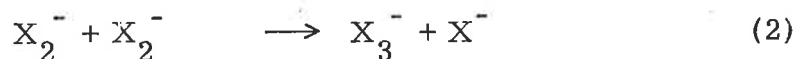
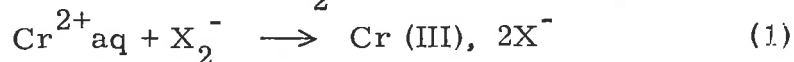
Addition of $5 \times 10^{-4} \text{ mol l}^{-1} \text{Cr}^{2+}_{\text{aq}}$ to deaerated acidified solutions of chloride, bromide or iodide removed any sign of X_2^{-} transient. On oxidation of the $\text{Cr}^{2+}_{\text{aq}}$ by air, transients were again observed. The weakly absorbing $\text{Cr}^{2+}_{\text{aq}}$ could not have so strong

an inner filter effect on the halide ions as to cause no X_2^- to be produced. The non observation of X_2^- is due to the very rapid removal of X or X_2^- before observation can take place, corresponding to an estimated half life for X_2^- removal of less than 10^{-5} s. The minimum value of the Cr^{2+} , X_2^- rate constant can therefore be estimated as $10^8 \text{ l mol}^{-1} \text{ s}^{-1}$. A faster detection time and in particular shorter response time of the apparatus (see 2.2.6) is required to measure the rates.

13.7.2 Measurement of Cr^{2+} aq, X_2^- rates.

The necessary measurements were performed by my supervisor Dr. G.S. Laurence during a period at Argonne National Laboratory using a nanosecond pulse radiolysis technique. The results are to be published in a paper by Laurence and Thornton (submitted to JCS Dalton.)

Under the experimental conditions ($10^{-3} - 10^{-2} \text{ mol l}^{-1}$ in Cr^{2+} aq) the decay of X_2^- was first order, the competition due to the second order disproportionation reaction (2) being insignificant at such high rates of removal of X_2^- .



From the dependence of the pseudo first order rate constant, k_1' , on Cr^{2+} aq the bimolecular rate constant, k_1 , can be calculated. The derived rate constants are given in Table 13.7A.

The measured rate constants are much greater than the lower limit of $10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ estimated from the preliminary flash photolysis experiments, (13.7.1)

Table 13.7A
Rates $\text{Cr}^{2+}_{\text{aq}} + \text{X}_2^-$

Reaction	Rate constant, k_1 $\times 10^{-9} \text{ l mol}^{-1} \text{ s}^{-1}$
$\text{Cr}^{2+}_{\text{aq}} + \text{Cl}_2^-$	2.4 ± 0.3
$\text{Cr}^{2+}_{\text{aq}} + \text{Br}_2^-$	1.9 ± 0.2
$\text{Cr}^{2+}_{\text{aq}} + \text{I}_2^-$	1.5 ± 0.2

13.7.3 Product observations, $\text{Cr}^{2+} + \text{I}_2^-$

The lack of long term stability* of the detection system at Argonne precluded observation on the nature of the initial products but even though rate measurements could not be made in Adelaide, it was possible due to the inertness of Cr (III) species to use techniques in which a sufficient concentration of $\text{Cr}^{2+}_{\text{aq}}$ to scavenge all X_2^- was used, and the final products observed.

A permanent ($t_{1/2} \sim 5$ min) absorbance was observed at 300 nm upon flash photolysis of a solution containing $10^{-3} \text{ mol l}^{-1} [\text{Cr}^{2+}_{\text{aq}}]$ and $10^{-1} \text{ mol l}^{-1} [\text{I}^-]$ at pH 1. The spectrum of the product measured using the flash photolysis detection system is shown in Figure 13.7A and compared with the measured spectrum of monoiodochromium (III) ion - $\text{Cr}(\text{H}_2\text{O})_5 \text{I}^{2+}$. The correspondence is excellent when the spectra are normalized. Assuming that all I_2^- produces $\text{CrI}^{2+}_{\text{aq}}$ and that the yield of I_2^- is the same in the presence and absence of $\text{Cr}^{2+}_{\text{aq}}$ the extinction coefficient of CrI^{2+} can be calculated to be $(3000 \pm 1000) @ 300 \text{ nm}$ in good agreement with our independently measured value from a spectrum which is in good agreement with that of Taube and Myers (1954), over their measured range.

*Footnote: A pulsed lamp was used to improve signal to noise ratios in short term detection but the stability of the pulsed light intensity over a period of 1 ms was consequently poor.

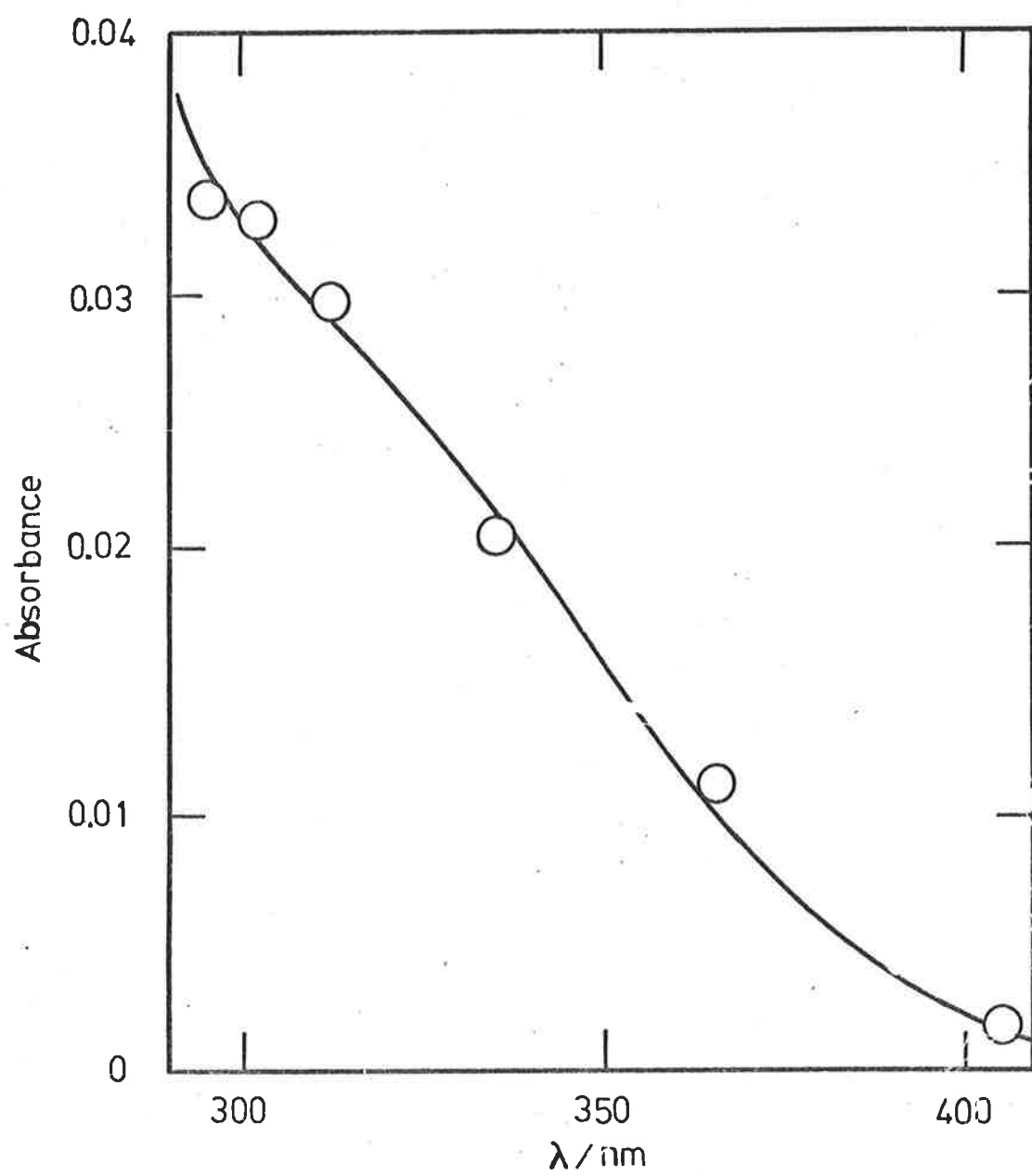
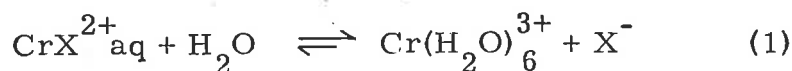


Fig. 13.7A Experimental Spectrum, $\text{CrI}^{2+}_{\text{aq}}$ (○)
Independently Measured Spectrum (—)

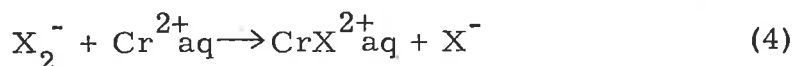
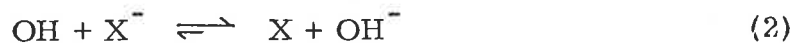
The high extinction bands of the corresponding bromo and chloro complexes are at innaccessibly short wavelengths for the flash photolysis detection system (see Fig. 12. 1A) and the observation of about $1 \mu\text{mol l}^{-1}$ concentrations of these species was impossible.

13.7.4 Steady irradiation, $\text{Cr}^{2+}_{\text{aq}} + \text{X}_2^-$

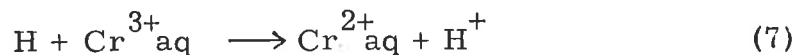
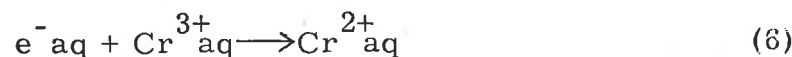
The chloro and bromochromium (III) complexes aquate only slowly in acid solution ($t_{1/2} \sim \text{days}$) (Guthrie and King, 1964; Baltisberger and King, 1964).



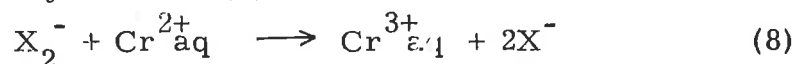
If they are formed as initial products in the radiolysis of $\text{Cr}^{2+}_{\text{aq}}, \text{X}^-$ solutions (Reactions (2) - (4)),



unless they are subsequently removed by another radical reaction, they will persist for a sufficiently long time to allow conventional detection. The chromium (III) products can be protected from subsequent attack by e^-_{aq} or H atoms by addition of an excess of $\text{Cr}^{3+}_{\text{aq}}$ which removes the reducing radicals (Anbar and Neta, 1967).



If reaction (4) proceeds as shown (inner sphere mechanism), radiolysis of a solution containing halide, acid, chromium (II) and aquochromium (III) will produce the monohalogenochromium (III) product at the expense of aquochromium (III). If, on the other hand, reaction of $\text{Cr}^{2+}_{\text{aq}}$ with X_2^- proceeds by reaction (8)



the above solutions will be stable to radiation.

Ion exchange separation of the products and subsequent spectrophotometric determination was used to identify and measure the yield of Cr (III) products. The expected yield of CrX^{2+} on the basis of 100% of X_2^- reacting by equation (4) was calculated from G values and dosimetry of the ^{60}Co source. By comparing the measured and expected yields of $\text{CrX}^{2+}_{\text{aq}}$ the percentage of X_2^- reacting by the inner sphere path (4) and the outer sphere path (8) can be calculated. The results are shown in Table 13.7B. The faster aquation rates of the $\text{CrI}^{2+}_{\text{aq}}$ and $\text{CrBr}^{2+}_{\text{aq}}$ products lead to larger uncertainties in the yields of inner and outer sphere products formed from Br_2^- and I_2^- . Aquation occurring during radiolysis or separation will result in an apparently higher percentage of outer sphere reaction.

Table 13.7B

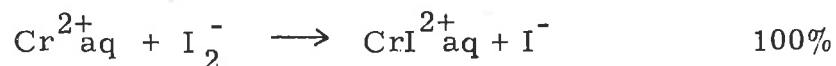
Reaction	$G(\text{X}_2^-)$	$G(\text{Cr X}^{2+}_{\text{aq}})$	% Inner Sphere
$\text{Cr}^{2+} + \text{Cl}_2^-$	2.6	1.22 ± 0.3^a	47 ± 10
$\text{Cr}^{2+} + \text{Br}_2^-$	2.6	2.10 ± 0.4^a	80 ± 15
$\text{Cr}^{2+} + \text{I}_2^-$	2.6	0.75 ± 0.4^b	29 ± 15

(a) 25°C

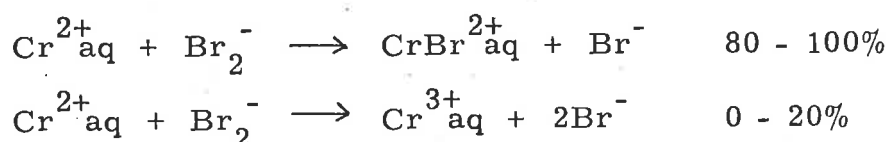
(b) 0°C

13.7.5 Mechanism, $\text{Cr}^{2+}_{\text{aq}} + \text{X}_2^-$

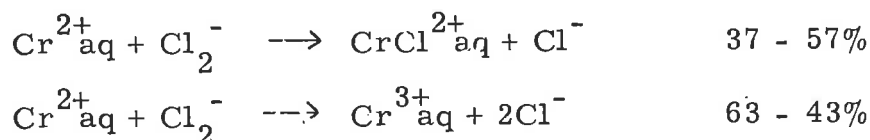
Product identification in the flash photolysis study of the $\text{Cr}^{2+}_{\text{aq}}, \text{I}_2^-$ reaction (13.7.3) suggests that the reaction is 100% inner sphere. The γ radiolysis results (13.7.4) do not contradict this finding when aquation of the $\text{CrI}^{2+}_{\text{aq}}$ product during the experiment is considered. (Espenson, 1964)



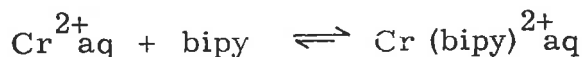
The γ radiolysis results for Br_2^- show that within the limits of experimental error, $G(\text{CrBr}^{2+})$ is the same as $G(\text{X}_2^-)$ (allowing for aquation of CrBr^{2+}). This does not rule out the possibility of a small proportion of the reaction (<20%) proceeding by an outer sphere mechanism but suggests that the reaction may be 100% inner sphere.



The limits of error on the steady γ radiolysis of the Cl_2^- , $\text{Cr}^{2+}_{\text{aq}}$ system are too small to account for the discrepancy from 100% inner sphere reaction. It is clear that the Cl_2^- , $\text{Cr}^{2+}_{\text{aq}}$ reaction proceeds by parallel inner and outer sphere paths.



The rate constants for oxidation of $\text{Cr}^{2+}_{\text{aq}}$ by X_2^- increase only slightly from I_2^- to Cl_2^- (see Table 13.7A). The rate constant for solvent exchange on $\text{Cr}^{2+}_{\text{aq}}$ is $\sim 8 \times 10^9 \text{ s}^{-1}$ (Meredith and Connick, 1965). Subject to restrictions due to the rate of diffusion of the reactants, the inner sphere $\text{Cr}^{\text{II}}\text{X}_2^+$ complexes could be formed at about this rate, but direct application of the Eigen mechanism involving ion-pair formation is invalid where the residence time of water molecules in the inner coordination sphere is about 10^{-10} s . The substitution rate of bipyridyl on $\text{Cr}^{2+}_{\text{aq}}$,



is $3.5 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$ (Diebler, 1970), considerably slower than solvent exchange but the rates of formation of chelate complexes are not necessarily good guides to the rate of substitution of monodentate anions. The observation of some inner sphere paths

in the $\text{Cr}^{2+}_{\text{aq}}, \text{X}_2^-$ redox reactions implies that at least some substitution takes place at a rate around $2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

The rate constants for the redox reactions are close to the upper limit set by diffusion of the reactants. If the reactions are not diffusion controlled then the inner sphere reactions of Br_2^- and I_2^- proceed at a substitution controlled rate of $1.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ and in a situation analogous to the $\text{Fe}^{2+}, \text{Cl}_2^-$ reaction which also exhibited duality of mechanism, the inner sphere path of the Cl_2^- , $\text{Cr}^{2+}_{\text{aq}}$ reaction might be expected to have a rate constant of $1.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. From the % inner sphere reaction the rate constant of the outer sphere path can be calculated as $1.8 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ and the total observed rate would be $3.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. It is clear that this rate is only partially attained ($k = 2.4 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) and consequently another process, diffusion, must be limiting the observed rate. The rate constants for Br_2^- and I_2^- are only slightly smaller than this and it is probable that these reactions are also diffusion controlled.

The reaction profiles for diffusion controlled outer sphere reactions are shown in Appendix 3.3 and 3.5. In each case the diffusion barrier is larger than the subsequent substitution or electron transfer barriers, and is equal for both mechanisms. Once the reactants diffuse together the substitution and/or redox reaction takes place without imposing a further limitation on the rate. The redox path subsequently followed depends upon whether the inner sphere or outer sphere path is energetically favourable, which in turn depends upon a balance between the ease of substitution and the ease of outer sphere electron transfer. In the Br_2^- and I_2^- cases where at least 90% reacts by an inner sphere path there must be at least 6 kJ mol^{-1} difference in the activation energies of the inner and outer sphere paths (only the inner sphere barrier need be less than the diffusion barrier). In the limit where electron transfer takes place at every

encounter (i. e. as soon as diffusion has occurred) the relative importance of the inner and outer sphere paths may depend solely on steric factors. $\text{Cr}^{2+}_{\text{aq}}$ is a very distorted octahedron. If the oxidant (X_2^-) approaches a vertex which is practically unoccupied inner sphere reaction may occur. If the oxidant approaches the more strongly bound equatorial positions outer sphere reaction may occur. On purely steric grounds the expected incidences of approach to the vertex or equator are about equal and one might expect ~50% inner sphere product and ~50% outer sphere product. This situation may be applicable to the reaction of Cl_2^- with $\text{Cr}^{2+}_{\text{aq}}$. It is not surprising that only Cl_2^- with the largest free energy change shows an outer sphere path.

13.7.6 Activation parameters

Although activation parameters have not been determined for the $\text{Cr}^{2+}_{\text{aq}}$, X_2^- reactions, the mechanisms have been deduced. Consequently the appropriate reaction profile can be constructed (see Appendices 3.3 and 3.5).

In each case the overall activation energy is that of the barrier to diffusion which is generally less than 12 kJ mol^{-1} .

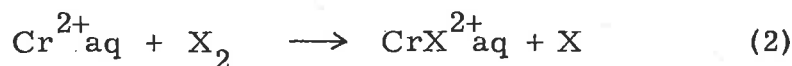
13.7.7 Literature comparisons

In their classic investigation of inner and outer sphere reactions of various complexes with $\text{Cr}^{2+}_{\text{aq}}$, Taube and Myers (1954) used the reaction of halogens with $\text{Cr}^{2+}_{\text{aq}}$ as a convenient method of producing $\text{CrBr}^{2+}_{\text{aq}}$ and $\text{CrI}^{2+}_{\text{aq}}$. The spectra of these species had not previously been reported and they established that the reactions could quantitatively be described as,

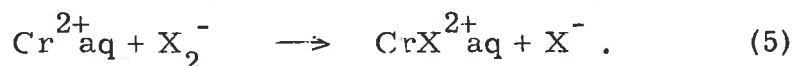
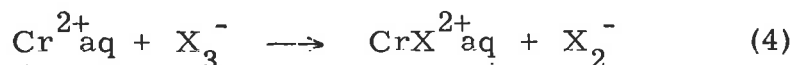


by observing that no free halide ion was present in the solution after reaction. In the reaction of chlorine with $\text{Cr}^{2+}_{\text{aq}}$

they found that only 75% of the Cl_2 appeared as CrCl^{2+} , the other 25% was as free chloride. They presumed that there must be a corresponding quantity of Cr^{3+} present in solution. This system was reinvestigated in more detail by Thompson and Gordon (1966) with substantially the same results. The halogens act as one electron reagents, and the reactions written in two steps, are

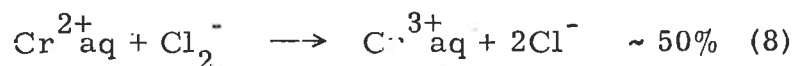
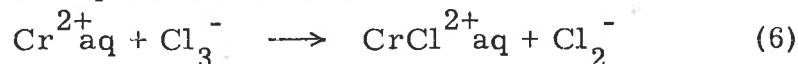


In the presence of excess halide ion the reaction scheme becomes



We have checked the results of Taube and Myers (1954) and Thompson and Gordon (1966) under the experimental conditions used in the γ radiolysis experiments (excess halide and acid). As shown in Table 13.7C excellent agreement is obtained.

It is apparent that in the case of Br_2 or I_2 reactions (2) and (3) or (4) and (5) adequately describe the mechanism but for Cl_2 (or Cl_3^-) there must be an extra path producing Cr^{3+} aq. In the reaction of Cl_2 with Cr^{2+} aq we have already found parallel inner and outer sphere paths of comparable rate and in view of this the reaction of Cl_3^- with Cr^{2+} aq should be written as



Reactions (6) to (8) predict 75% of the product should be CrCl^{2+} aq and 25% Cr^{3+} aq in excellent agreement with the experimentally observed ratios. These results are in quantitative agreement with

Table 13.7C

 $\text{Cr}^{2+}_{\text{aq}}$, X_3^- reactions

Reaction	% $\text{CrX}^{2+}_{\text{aq}}$		
	a	b	c
$\text{Cr}^{2+}_{\text{aq}} + \text{Cl}_2$	78	75	$74 \pm 5^*$
$\text{Cr}^{2+}_{\text{aq}} + \text{Br}_2$	-	100	$98^\dagger$
$\text{Cr}^{2+}_{\text{aq}} + \text{I}_2$	-	100	$95^\dagger$

(a) Thompson and Gordon (1966)

(b) Taube and Myers (1954)

(c) Current work

* $26 \pm 5\%$ $\text{Cr}^{3+}_{\text{aq}}$ † The discrepancy from 100% is attributable to aquation of $\text{CrX}^{2+}_{\text{aq}}$ during separation.

the previous observations on the $\text{Cr}^{2+}_{\text{aq}}$, X_2^- reactions.

The rate constant for the $\text{Cl}_2, \text{Cr}^{2+}_{\text{aq}}$ reaction has been measured by Thompson and Gordon as $(9.7 \pm 0.3) \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ at $I = 0.1 - 0.5 \text{ mol l}^{-1}$ and $T = 5^\circ\text{C}$. This rate is very much slower than the reactions of X_2^- with $\text{Cr}^{2+}_{\text{aq}}$ and it is clear that the initial inner sphere step in the oxidation of $\text{Cr}^{2+}_{\text{aq}}$ by Cl_2 is rate determining (reaction 6). The rate is so much slower than the substitution rate on $\text{Cr}^{2+}_{\text{aq}}$ ($\sim 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) that reaction (6) must be limited by the rate of electron transfer.

The γ radiolysis of solutions of $\text{Cr}^{2+}_{\text{aq}}$ and chloride ions has been investigated by Lykourezas, Kanellopoulos and Katakis (1968). They measured the yields of $\text{CrCl}^{2+}_{\text{aq}}$, $\text{Cr}^{3+}_{\text{aq}}$ and dimeric chromium (III) species at varying chloride and perchloric acid concentrations. They used perchloric acid concentrations up to 2.8 mol l^{-1} at which concentration significant radiolytic decomposition of the perchlorate ion was occurring. As the perchlorate concentration increased so the yield of $\text{CrCl}^{2+}_{\text{aq}}$ increased, well above the maximum obtainable yield from Cl_2^- . It appears that the radiolytic products from perchlorate also produce $\text{CrCl}^{2+}_{\text{aq}}$ from $\text{Cr}^{2+}_{\text{aq}}$. Their G value for $\text{CrCl}^{2+}_{\text{aq}}$, at $0.4 \text{ mol l}^{-1} \text{ Cl}^-$ and $0.56 \text{ mol l}^{-1} \text{ HClO}_4$ (the conditions closest to our experimental conditions) was 2.8, about twice as high as our measured G value at $0.2 \text{ mol l}^{-2} \text{ HClO}_4$. It is apparent that even at 0.5 mol l^{-1} , perchlorate undergoes significant radiolytic decomposition in the absence of added hydrogen atom scavengers. Little comparison can be made between our results in which $\text{Cr}^{3+}_{\text{aq}}$ was added to scavenge hydrogen atoms and their results in which the hydrogen atom decomposition of perchlorate was significant.

13.8 VANADIUM (II)

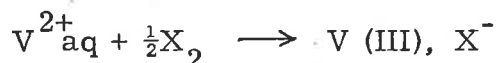
V^{2+} is readily oxidised in aqueous solution.



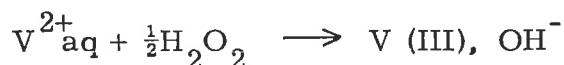
Reaction with all three radical anions is energetically favourable



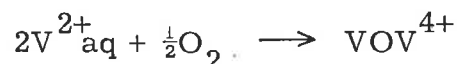
V^{2+}_{aq} reacts rapidly with halogens (Malin and Swinehart, 1969)



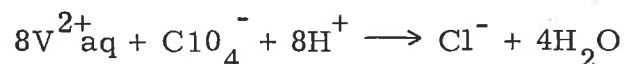
with hydrogen peroxide (Swinehart, 1965)



with oxygen (Swinehart, 1965)



and is reported to react slowly with perchlorate (King and Garner, 1954)



although no complication due to this reaction was experienced at ambient temperatures.

As with Cr^{2+}_{aq} only deaerated or N_2O saturated halide solutions are suitable for study of V^{2+}_{aq} , $X_2^{-\cdot}$ reactions.

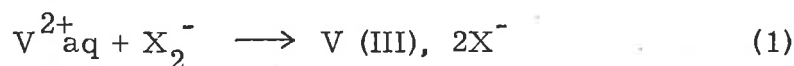
13.8.1 Preliminary rate measurements

Transfer and handling of very dilute ($< 5 \times 10^{-4} \text{ mol l}^{-1}$) V^{2+}_{aq} solutions is extremely difficult due to interference from trace amounts of oxygen. The resulting concentration is not sufficiently reliable to obtain a reasonable rate measurement. As with Cr^{2+}_{aq} (13.7.1) addition of $\sim 5 \times 10^{-4} \text{ mol l}^{-1}$ concentrations of V^{2+}_{aq} to deaerated chloride, bromide or iodide removed any $X_2^{-\cdot}$ transient in the time of the flash. The minimum value of the V^{2+}_{aq} , $X_2^{-\cdot}$ rate

constant is therefore estimated at $10^8 \text{ l mol}^{-1} \text{ s}^{-1}$.

13.8.2 Measurement of V^{2+} , X_2^- rates.

The necessary measurements were again performed by Dr. G.S. Laurence using the nanosecond pulse radiolysis facility at Argonne National Lab. The results are to be published in the same paper as the chromium (II) results (Laurence and Thornton; submitted to JCS Dalton). From the dependence of the observed pseudo first order rate constants, k_1' on $[V^{2+}_{aq}]$ the bimolecular rate constants k_1 can be calculated.



The values are listed in Table 13.8A.

Table 13.8A

Rates $V^{2+}_{aq} + X_2^-$

Reaction	Rate constant k_1 $\times 10^{-9} \text{ l mol}^{-1} \text{ s}^{-1}$	$-\Delta G^\circ$ kJ mol^{-1}
$V^{2+}_{aq} + Cl_2^-$	1.95 ± 0.2	241
$V^{2+}_{aq} + Br_2^-$	1.48 ± 0.2	191
$V^{2+}_{aq} + I_2^-$	0.143 ± 0.02	116

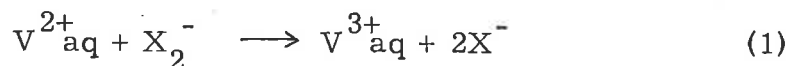
13.8.3 Product observations

Product observations are not feasible on the pulse radiolysis facility at Argonne due to the use of pulsed monitoring lamps. $V(III)$ is known to be fairly labile ($k_{H_2O_{ex}} \approx 10^2 \text{ s}^{-1}$; Kruse and Thusius, 1968; Sutin, Baker and Welch, 1967) and although flash photolysis detection of products may be possible, product isolation and analysis is not. Unequivocal definition of the mechanism of V^{2+}_{aq} , X_2^- reactions does not require product observations (see 13.8.4), which were consequently not performed.

13.8.4 Mechanism $V^{2+}_{aq} + X_2^-$

The rates of formation and aquation of vanadium (II) complexes are relatively slow. The rate of substitution of SCN^- ions on V^{2+}_{aq} is about $28 \text{ l mol}^{-1} \text{ s}^{-1}$ at 25°C (Malin and Swinehart, 1968; Kruse and Thusius, 1968; Baker, Orhanovic and Sutin, 1967) and the rate of water exchange on V^{2+}_{aq} ions is 90 s^{-1} (Olson, Kanazawa and Taube, 1969). The rates of substitution of X_2^- radical anions on other divalent transition metal aquo ions are approximately the same as the rates of substitution of simple anions. (13.1.4, 13.2.3). Halogen radical anions are therefore likely to substitute on V^{2+}_{aq} ions with rate constants $\sim 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$, six or seven orders of magnitude slower than the observed rates of oxidation of V^{2+}_{aq} ions by X_2^- .

The reactions with halogen radical anions must proceed by an outer sphere mechanism (1).



In section 11.4.1 outer sphere reactions of transition metal ions with simple anions such as X_2^- were discussed and an inverse dependence of the rate on the free energy change was predicted. This trend is apparent with the $V^{2+}_{aq} X_2^-$ reactions but the rates appear to approach an upper limit as the reactions become more exothermic (Table 13.8A). This apparent limit of $\sim 2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ is very close to the expected diffusion limit and the observed diffusion limit ($\sim 2.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$) in the Cr^{2+}_{aq}, Cl_2^- reaction. This approach to a limit has been discussed by Marcus (1968), who predicts

$$1/k_{\text{obs}} = 1/k_{\text{et}} + 1/k_{\text{diff}}$$

where

k_{obs} = observed rate constant

k_{et} = hypothetical electron transfer rate constant in the absence of diffusion limit

k_{diff} = limiting diffusion rate constant

For Br_2^- and Cl_2^- whose electron transfer rates might be

expected to differ by a factor of 10, $1/k_{\text{diff}}$ is the dominant term, but for I_2^- , $1/k_{\text{et}}$ is dominant due to the lower electron transfer rate.

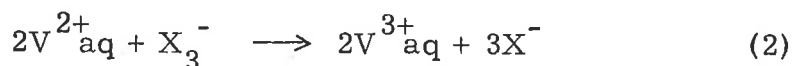
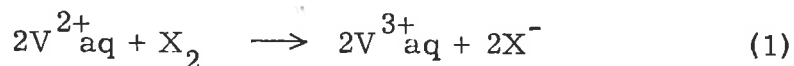
13.8.5 Activation Parameters

Activation parameters for $\text{V}^{2+}_{\text{aq}}$, X_2^- reactions were not measured but from the mechanisms the type of reaction profile can be deduced. $\text{V}^{2+}_{\text{aq}}$, I_2^- reaction follows the typical outer sphere profile given in Appendix 3.4 whilst for Cl_2^- and Br_2^- the barrier to electron transfer has dropped below the barrier to diffusion and the profile in Appendix 3.5 is observed.

13.8.6 Literature comparison

The reactions of halogens and trihalide ions with vanadium (II) are proposed to proceed through halogen radical anions as intermediates (Malin and Swinehart, 1969). The rates are between 10 and 10^3 times faster than the rate of substitution on $\text{V}^{2+}_{\text{aq}}$ (see Table 13.8B).

The authors do not rule out the possibility of an inner sphere reaction in which the presence of the incoming ligand assists the substitution. Such a large increase in the substitution rate is most unusual, particularly for an incoming neutral ligand, and it is probable that an outer sphere reaction operates:



The $\text{V}^{2+}_{\text{aq}}$, halogen rate constants show little dependence on the free energy change for the reaction (Table 13.8B). In section 11.4.1 such a dependence was predicted for outer sphere reactions between transition metal complexes and simple neutral molecules. This lack of dependence and the unusually low enthalpies and entropies of activation suggest that the reaction may be more complex than envisaged, a conclusion supported by other observations on the system. (See below.)

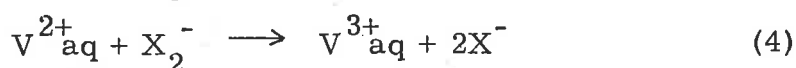
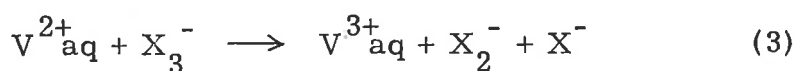
Table 13.8B

Rates and Activation Parameters, $V^{2+}_{aq} + X_2$

(Malin and Swinehart, 1969)

Reaction	k_{25° ($l\ mol^{-1}\ s^{-1}$)	$\Delta H^\ddagger$ $kJ\ mol^{-1}$	$\Delta S^\ddagger$ $J\ mol^{-1}\ K^{-1}$	$-\Delta G^\circ$ $kJ\ mol^{-1}$
$V^{2+} + I_3^-$	$(9.7 \pm 0.2) \times 10^2$	38 ± 1	-59 ± 5	50
$V^{2+} + I_2$	$(7.5 \pm 0.5) \times 10^3$	25 ± 2	-88 ± 8	50
$V^{2+} + Br_2$	$(3 \pm 0.4) \times 10^4$	15 ± 4	-110 ± 16	125
$V^{2+} + Cl_2$	$>5 \times 10^2$	-	-	150

Halogens are recognized as one electron oxidisers, X_2^- being an intermediate in the reduction to halide. Malin and Swinehart as expected observed no V (IV) in the products of the V (II), halogen reactions. In one electron steps the oxidation of V^{2+}_{aq} by halogens can be written



We have measured the rate constants of reaction (4) and found them to be at least 10^4 times faster than the overall reaction. In agreement with Malin and Swinehart it is concluded that reaction (3) is rate limiting.

Malin and Swinehart observed an interference due to transient absorbance in the 300 - 400 nm region in the study of the V^{2+}_{aq} , Br_2 and V^{2+}_{aq} , Cl_2 reactions. They attributed this to X_2^- which complicated their decay curves due to its absorbance in the wavelength region. From their values of k_3 and our values of k_4 the steady state concentration of X_2^- at any time can be calculated. Under their initial conditions the steady state $[X_2^-]$ is $\sim 10^{-9}$ mol l^{-1} , corresponding to a completely undetectable absorbance of about 10^{-5} in a 1 cm cell. The cause of interference in their kinetic plots is certainly not X_2^- . Another intermediate species must therefore be responsible for the anomalous absorbance, and the low activation energies may indicate an undetected equilibrium step involving this intermediate.

13.9 COMPARISON OF VARIOUS DIVALENT TRANSITION METAL AQUO IONS

Table 13.9A lists the various mechanisms observed for oxidation of the divalent first row transition metal aquo ions by halogen radical anions. The reactions studied display a wide variety of free energy changes from -22 kJ mol^{-1} for Fe^{2+}_{aq} and I_2^- to -263

Table 13.9A

Rates and mechanisms of $M^{2+} + X_2^-$ ($X = I, Br, \text{ or } Cl$) reactions

Reaction	Mechanism ^a	ΔG° (kJ mol ⁻¹)	$k_{25^\circ C}$ (1 mol ⁻¹ s ⁻¹)	k_{H_2O} exchange (s ⁻¹)
$V^{2+} + Cl_2^-$ ^b	OS-diffusion	-241	$(1.95 \pm 0.2) \times 10^9$	0.9×10^2 ^g
$V^{2+} + Br_2^-$ ^b	OS-diffusion	-191	$(1.48 \pm 0.2) \times 10^9$	
$V^{2+} + I_2^-$ ^b	Outer-sphere	-116	$(1.43 \pm 0.2) \times 10^8$	
$Cr^{2+} + Cl_2^-$ ^b	OS-diffusion	-263	$(2.4 \pm 0.3) \times 10^9$	8×10^9 ^h
$Cr^{2+} + Cl_2^-$ ^b	IS-diffusion	-263	$(2.4 \pm 0.3) \times 10^9$	
$Cr^{2+} + Br_2^-$ ^b	IS-diffusion	-213	$(1.9 \pm 0.2) \times 10^9$	
$Cr^{2+} + I_2^-$ ^b	IS-diffusion	-138	$(1.5 \pm 0.2) \times 10^9$	
$Mn^{2+} + Cl_2^-$ ^c	IS-electron transfer	-75	8.5×10^6	2.3×10^7 ⁱ
$Mn^{2+} + Br_2^-$ ^c	IS-electron transfer	-25	6.3×10^6	
$Fe^{2+} + Cl_2^-$ ^d	Outer-sphere	-147	1.0×10^7	3.2×10^6 ^j
$Fe^{2+} + Cl_2^-$ ^d	IS-substitution	-147	4.0×10^6	
$Fe^{2+} + Br_2^-$ ^d	IS-substitution	-97	3.6×10^6	
$Fe^{2+} + I_2^-$ ^e	IS-substitution	-22	3.6×10^6	
$Co^{2+} + Cl_2^-$ ^f	IS-substitution	-33	1.4×10^6	2×10^6 ^k

- (a) OS-diffusion and IS-diffusion refer to the outer-sphere and inner-sphere diffusion controlled mechanisms respectively. IS-electron transfer and IS-substitution refer to the inner-sphere electron transfer controlled and inner-sphere substitution controlled mechanisms respectively.
- (b) This work. Activation parameters were not determined for these diffusion controlled reactions.
- (c) G.S. Laurence and A.T. Thornton, J.C.S. Dalton, to be published.
- (d) A.T. Thornton and G.S. Laurence, J.C.S. Dalton, 1973, 804.
- (e) G.S. Laurence, unpublished data.
- (f) A.T. Thornton and G.S. Laurence, J.C.S. Dalton, to be published.
- (g) M. Olson, Y. Kanazawa, and H. Taube, J. Chem. Phys., 1969, 51, 289.
- (h) C.W. Meredith and R.E. Connick, Abstracts, 149th Meeting of the American Chemical Society, Detroit, 1965, Abstract 108 M.
- (i) M. Grant, H.W. Dodgen, and J.P. Hunt, Inorg. Chem., 1971, 10, 71.
- (j) T.J. Swift and R.E. Connick, J. Chem. Phys., 1962, 37, 307.
- (k) J.P. Hunt, Co-ordination Chem. Rev., 1971, 7, 1.

kJ mol^{-1} for $\text{Cr}^{2+}_{\text{aq}}$ and Cl_2^- . The various metal ions differ substantially in their lability with water exchange rate constants of 90 s^{-1} for $\text{V}^{2+}_{\text{aq}}$ to $\sim 8 \times 10^9 \text{ s}^{-1}$ for $\text{Cr}^{2+}_{\text{aq}}$. It is not surprising that the reactions show such a variety of mechanisms. To rationalize the incidence of a particular mechanism the intimate details of each reaction must be considered.

Outer sphere reactions have been treated theoretically by Marcus (1964) and to a first approximation the barrier to electron ($\Delta E^\ddagger_{34}$ in Appendix 3.4) is composed of 4 terms

$$E_{\text{et}} = E_{\text{electr}} + E_{\text{r}} + E_{\text{s}} + E_{\text{sp}}$$

where E_{et} = activation energy for electron transfer

E_{electr} = the energy necessary to overcome electrostatic barriers to reaction

E_{r} = energy necessary to reorganize molecular dimensions prior to the transition state

E_{s} = energy necessary to reorganize

E_{sp} = energy necessary to reorganize spin state

For all reactions between divalent metal ions and halogen radical anions the electrostatic and solvent reorganization terms, E_{electr} and E_{s} , might be expected to be similar.

E_{sp} , spin reorganization energy, arises from the necessity to invert electronic spins to reach the final ground state or an intermediate excited spin state and will of course vary with the electronic configurations. Stynes and Ibers (1971) for example, propose that the electron exchange between Co (II) and Co (III) hexaammines is limited by the magnitude of this term ($\sim 100 \text{ kJ mol}^{-1}$). Consideration only of the spin reorganization in going from ground state reactant to ground state product ignores the possibility of an excited spin state intermediate or transition state and assumes

that either an e_g or a t_{2g} electron can be removed at will. For example oxidation of $Cr^{2+}aq$ to $Cr^{3+}aq$ requires removal of an e_g electron whereas oxidation of $Fe^{2+}aq$ to $Fe^{3+}aq$ requires removal of t_{2g} electron. All reactions studied involve X_2^- either bonded to (inner sphere mechanism) or adjacent to (outer sphere mechanism) the metal centre. Particularly in the inner sphere situation where electron transfer takes place through the primary bond system (Taube 1970) one would expect orbital symmetry considerations to impose restrictions on the type of electron that could be donated, leading to the possibility of excited spin state intermediates. Prediction of restrictions requires knowledge of the nature of the orbitals and bonding of X_2^- and the degree of influence of the metal on the energy levels of the ligand orbitals, but unfortunately such data are not available.

Table 13.9B shows the electron configurations resulting from the removal of an e_g or a t_{2g} electron from the metal ion and cases where a subsequent spin change is required to reach the final ground state product.

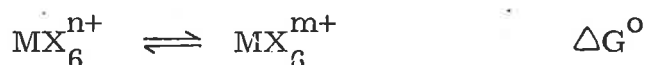
Only in the oxidation of $Co^{2+}aq$ to $Co^{3+}aq$ is a spin change certain to be necessary. For the other metal ions a spin change may be necessary if the electron removed is not the one leading to ground state product directly. The reaction between $Co^{2+}aq$ and Cl_2^- is inner sphere substitution controlled. The barrier to the electron transfer cannot be directly obtained but must be less than the observed activation energy ($\sim 34 \text{ kJ mol}^{-1}$). It is apparent that the magnitude of the spin reorganization term for this reaction is considerably less than the 100 kJ mol^{-1} experienced in the $Co(II)$, $Co(III)$ hexaammine exchange reaction. If spin change does not limit the $Co^{2+}aq$ oxidation it is unlikely that by itself the E_{sp} term could limit the rate of oxidation of any of the other divalent metal ions.

Table 13.9B
Electron Configurations

M	M^{2+}_{aq}	$-e_g$	spin change	$-t_{2g}$	spin change	M^{3+}_{aq}
V	t_{2g}^3	-	-	t_{2g}^2	no	t_{2g}^2
Cr	$t_{2g}^3 e_g^1$	t_{2g}^3	no	$t_{2g}^2 e_g^1$	yes	t_{2g}^3
Mn	$t_{2g}^3 e_g^2$	$t_{2g}^3 e_g^1$	no	$t_{2g}^2 e_g^2$	yes	$t_{2g}^3 e_g^1$
Fe	$t_{2g}^4 e_g^2$	$t_{2g}^4 e_g^1$	yes	$t_{2g}^3 e_g^2$	yes	$t_{2g}^3 e_g^2$
Co	$t_{2g}^5 e_g^1$	$t_{2g}^5 e_g^1$	yes	$t_{2g}^4 e_g^2$	yes	t_{2g}^6
Ni	$t_{2g}^6 e_g^2$	$t_{2g}^6 e_g^1$	?	$t_{2g}^5 e_g^2$	?	?

It may however be a significant component of E_{et} in situations where the necessary reorganization ($E_r + E_s$) is the primary barrier to electron exchange.

E_r the energy necessary to reorganize molecular dimensions depends upon the difference in the geometries and dimensions of reactants and transition state and upon the free energy change for the reaction. On the assumption of negligible overlap between reactants and products and applying the restriction imposed by the Franck-Condon principle that no change in bond lengths takes place during electron transfer, the average bond length in the transition state for a reaction of the type



can be calculated (See Footnote (a))

$$r^\ddagger = \frac{k_m r_m - k_n r_n - \left[\frac{\Delta G^0}{3} (k_m - k_n) + k_m k_n (r_m - r_n)^2 \right]^{\frac{1}{2}}}{k_m - k_n}$$

The energy required to reach the transition state i. e. the reorganization energy of MX_6^{n+} is given by

$$\begin{aligned} E_r &= 6\left(\frac{1}{2} k_n (r^\ddagger - r_n)^2\right) \quad (\text{See Footnote (b)}) \\ &= 3k_n (r^\ddagger - r_n)^2 \end{aligned}$$

Footnotes:

(a) $m = n + 1$ refer to oxidation states

k is the force constant of M-X bond

r is the length of M-X bond

ΔG^0 is the overall free energy change

In the situation where $\Delta G^0 = 0$ (e. g. an exchange reaction) the expression reduces to

$$r^\ddagger = \frac{k_m^{\frac{1}{2}} r_m + k_n^{\frac{1}{2}} r_n}{k_m^{\frac{1}{2}} + k_n^{\frac{1}{2}}}$$

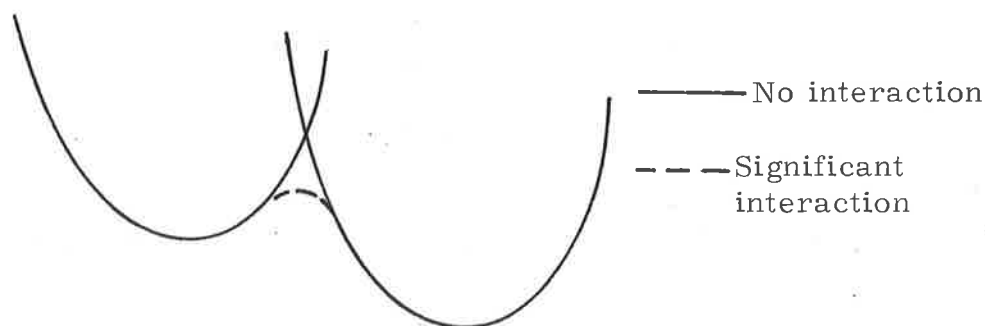
identical with the expression used by Stynes and Ibers (1971).

(b) The factor 6 arises because each of the M-X bonds is assumed to expand or contract equally.

If the other reactant responsible for the oxidation is also subject to bond length changes then using the assumption of no interaction in the transition state, the overall reorganization energy is the summation of the individual reorganization energies for the reactants. The major limitation to the applicability of these expressions is overlap or interaction in the transition state. If significant interaction between reactants and products occurs in the transition state then conversion between two hypothetical states of equal energy with, but on either side of, the transition state is presumably rapid (Marcus, 1956). Heisenberg's uncertainty principle implies the uncertainty in the energy of the transition state, ΔE , and the time taken for interconversion, t , are inversely related.

$$t \cdot \Delta E = h/4$$

In terms of a physical picture this uncertainty is represented by a tunnelling mechanism with the resultant diminution of the energy barrier.



In his discussion of limitations posed by the uncertainty principle Marcus (1956) suggests that the interconversion time in outer sphere reactions is likely to be long relative to that in inner sphere reactions where interaction or overlap is stronger. The uncertainty in energy states must therefore be larger for inner sphere

reactions and the theory less applicable. With some assumptions and in the absence of any better way of treating electron transfer controlled innersphere reactions, the expressions can be used to estimate the magnitude of the E_r term for the reactions of X_2^- with M^{2+}_{aq} .

Necessary assumptions are:

- (1) negligible overlap occurs in the transition state
- (2) E_r for reorganization of X_2^- is negligible
- (3) coordinated X_2^- molecules behave in the same manner towards reorganization as coordinated H_2O .
- (4) Force constants for $M(III) - O$ and $M(II) - O$ bonds are 1.7×10^5 and 0.7×10^5 dyne cm^{-1} respectively.
- (5) Because bond length data for many of the $M(H_2O)_6^{n+}$ complexes are not available, bond length data for $M - O$ bonds in other complexes containing oxygen ligands (see Table 13.9C) are used.

The predicted reorganization energies are listed in Table 13.9D.

To obtain the overall activation energy for the electron transfer (E_{et}) the spin term (E_{sp}), the electrostatic term (E_{electr}), and the solvent reorganization term (E_s) must be added to the calculated E_r value. The absolute magnitude of these terms is not known but comparing similar reactions, relative magnitudes can be estimated.

Table 13.9C

M - O bond length data

Bond	Reference	compound	r_{O} (Å)	ave r_{O} (Å)	$r_{\text{II}} - r_{\text{III}}$ (Å)	
Mn(II)-O	a	Mn(acac) ₂ (H ₂ O) ₂	2.13	2.16	0.28	
	b	Mn(H ₂ O) ₂ Cl ₂	2.15			
	c	Mn(H ₂ O) ₄ Cl ₂	2.21			
Mn(III)-O*	d	Mn(acac) ₃	1.87	1.88		
	e	MnO(OH)	1.88			
Co(II)-O	b	Co(H ₂ O) ₂ Cl ₂	2.04	2.05	0.14	
	f	Co(acac) ₂ (H ₂ O) ₂	2.055			
	g	Co(acac) ₂	2.055			
Co(III)-O	h	Co(acac) ₃	1.91	1.91		
	i	Co(NO ₃) ₃	1.90			
Fe(II)-O	b	Fe(H ₂ O) ₂ Cl ₂	2.07	2.08	0.05	
	j	Fe(H ₂ O) ₄ Cl ₂	2.09			
Fe(III)-O	k	Fe(H ₂ O) ₆ Cl ₃	2.07	2.03		
	l	Fe(acac) ₃	1.99			

Notes Table 13.9C

*Distances quoted are for the 4 shorter M - O bonds. In $\text{MnO}(\text{OH})$ two more oxygens are at $2.30\text{\AA}$.

acac = acetylacetone

References:

- (a) Montgomery & Lingafelter (1968)
- (b) Morison & Graebner (1965)
- (c) Zalkin, Forrester & Templeton (1964)
- (d) Morison & Brothovde (1964)
- (e) Cotton & Wilkinson (1967)
- (f) Bullen (1959)
- (g) Cotton & Elder (1965)
- (h) Padmanabhan (1958)
- (i) Hilton & Wallwork (1968)
- (j) Penfold & Grigor (1959)
- (k) Lind (1968)
- (l) Iball & Morgan (1967)

Table 13.9D

Reorganization energies

Reaction	$-\Delta G^\circ$ kJ mol ⁻¹	$r^\ddagger$ Å	$r^\ddagger - r_{II}$ Å	E_r kJ mol ⁻¹
$\text{Mn}(\text{H}_2\text{O})_5\text{Br}_2^+ \rightleftharpoons \text{Mn}(\text{H}_2\text{O})_5\text{Br}^{2+}$	25	2.01	0.15	28
$\text{Mn}(\text{H}_2\text{O})_5\text{Cl}_2^+ \rightleftharpoons \text{Mn}(\text{H}_2\text{O})_5\text{Cl}^{2+}$	75	2.05	0.11	15
$\text{Fe}(\text{H}_2\text{O})_5\text{I}_2^+ \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_5\text{I}^{2+}$	22	*	0	0
$\text{Fe}(\text{H}_2\text{O})_5\text{Br}_2^+ \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_5\text{Br}^{2+}$	97	*	0	0
$\text{Fe}(\text{H}_2\text{O})_5\text{Cl}_2^+ \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$	147	*	0	0
$\text{Co}(\text{H}_2\text{O})_5\text{Cl}_2^+ \rightleftharpoons \text{Co}(\text{H}_2\text{O})_5\text{Cl}^{2+}$	43	2.03	0.02	0.6

Notes

* Potential energy surfaces for bond stretching of reactants and products do not intersect between r_{reactant} and r_{product} . The barrier due to reorganization is more than compensated for by the free energy change:- $E_r = 0$.

$\ddagger$ Transition state

The free energy changes in halogen radical anion reactions are relatively large and the reorganizational terms are consequently small. Only Mn(II) shows a significant barrier to electron transfer due to the need to reorganize inner coordination spheres. Qualitatively this barrier can be understood in terms of electron configurations. $\text{Mn}^{2+}_{\text{aq}}$ has the configuration of high spin d^5 ($t_{2g}^3 e_g^2$), $\text{Mn}^{3+}_{\text{aq}}$ has the configuration of high spin d^4 ($t_{2g}^3 e_g^1$). In the d^4 situation only one of the e_g orbitals is occupied and Jahn Teller splitting occurs to minimize the energy. This splitting results in tetragonal distortion of the octahedral symmetry with the result that compared with the undistorted $\text{Mn}^{2+}_{\text{aq}}$ situation, the four equatorial ligands in $\text{Mn}^{3+}_{\text{aq}}$ are considerably closer and the two axial ligands are more distant.

This distortion is seen in the Mn (III) -O bond lengths (Table 13.9C). The contraction necessary to go from Mn (II) -O to Mn (III) -O is significantly larger than for Fe (II) or Co (II). Table 13.9D shows the effect of this on the E_r term which is significantly greater for Mn (II) than Fe (II) or Co (II).

The reactions of Fe (II) and Co (II) with halogen radical anions are inner sphere substitution controlled. The major barrier in the redox reaction is that of substitution. The subsequent electron transfer barrier is smaller, (see Appendix 3.2) and except in the case of $\text{Fe}^{2+}_{\text{aq}} + \text{Cl}_2^-$ the barrier to outer sphere reaction, which is not observed, is significantly larger. In the case of $\text{Mn}^{2+}_{\text{aq}}$ the additional barrier due to reorganization (Table 13.9D) is apparently sufficient to raise the electron transfer barrier above the substitution barrier because the reactions are inner sphere electron transfer controlled (Appendix 5.1).

Although the explanation rationalizes the occurrence of an inner sphere electron transfer controlled mechanism on $\text{Mn}^{2+}_{\text{aq}}$ it does not explain why the Cl_2^- and Br_2^- rates are very similar.

Reorganization terms would require a difference of 13 kJ mol^{-1} in the activation energies of the two reactions, corresponding to relative rates of about 200:1 for the electron transfer step, a difference which is clearly not observed. One is forced to conclude either that in the reaction of Mn^{2+}aq with Cl_2^- some additional barrier (relative to the Mn^{2+}aq , Br_2^- barrier) is responsible for compensating the observed activation energy to the extent of $\sim 13 \text{ kJ mol}^{-1}$, or that reorganization is not the significant barrier to inner sphere electron transfer on Mn^{2+}aq , above that for substitution.

The reactions of V^{2+}aq with X_2^- are the only reactions which proceed entirely by an outer sphere mechanism. The substitution barrier on V^{2+}aq is at least 20 kJ mol^{-1} larger than that for the other divalent metal ions studied (Olson, Kanazawa and Taube, 1969), and the barrier to outer transfer electron transfer is relatively small due to the favourable free energy changes. One would expect that if the Marcus free energy relationship ($\Delta G^\ddagger \propto \Delta G^0$) is applicable to any of the X_2^- reactions that they would be applicable to the reactions of V^{2+}aq . However, diffusion poses an upper limit to the rates and the full electron transfer rate constants for Br_2^- and Cl_2^- are not attained (see 13.3.4), consequently a meaningful linear free energy plot cannot be constructed. Qualitatively one can say that for V^{2+}aq reactions as ΔG^0 increases the rate constant increases and $\Delta G^\ddagger$ decreases, as expected.

The outer sphere component of the Fe^{2+} , Cl_2^- reaction does not fit the qualitative correlation observed for V^{2+}aq reactions. The free energy change, $-\Delta G^0$, is about 30 kJ mol^{-1} larger for Fe^{2+}aq , Cl_2^- than for V^{2+}aq , I_2^- and the rate, which would therefore be expected to be larger, is a factor of 10 smaller. Some additional barrier relative to that in outer sphere V^{2+}aq , X_2^- reactions must exist in the outer sphere reaction of Fe^{2+}aq with Cl_2^- . Table 13.9D lists the

expected magnitude of the molecular rearrangement energy term, E_r , for reaction of Fe^{2+}aq with Cl_2^- . It is apparent that this term cannot be responsible for the barrier in the $\text{Fe}^{2+}\text{aq}, \text{Cl}_2^-$ reaction. It seems equally improbable that differences in E_{electr} or E_s could account for the observed discrepancy. The spin term, E_{sp} , only imposes a barrier to the Fe^{2+} reaction if an e_g electron must be removed (see Table 13.9B). Although the removal of an e_g electron can be rationalized by orbital requirements it seems most unlikely that the barrier to removing an e_g electron from V^{2+}aq , which has only t_{2g} electrons in the ground state, would be less than the barrier to removal of an e_g electron from Fe^{2+}aq . The reason for the additional barrier to outer sphere electron transfer on Fe^{2+}aq (relative to V^{2+}aq) cannot be attributed to any particular one of the terms involved in E_{et} .

The usefulness of the Marcus free energy relationship in describing the rates of X_2^- reactions is limited. The reactions of Cr^{2+}aq with X_2^- and V^{2+}aq with Cl_2^- and Br_2^- are diffusion controlled. The majority of the remaining reactions are inner sphere substitution controlled and their rates cannot be correlated with free energy changes. Some are inner sphere electron transfer controlled and although the Marcus theory has in some instances been reasonably successfully applied to such cases (Sutin, 1966) there is no reason why it should, as the basic assumption of negligible interaction cannot be justified for this mechanism. The only reactions that could reasonably be expected to obey a Marcus free energy relationship are the outer sphere reactions and even there, although a positive correlation between free energy and rate constant is observed for the vanadium (II) reactions, the iron (II), Cl_2^- rate constant does not fit the same correlation.

The reactions of halogen radical anions with divalent metal ions are predominantly inner sphere. With the use of fast reaction techniques the importance of inner sphere reactions on labile metal

ions is becoming apparent (McAuley, 1970). The halogen radical anion reactions discussed here are direct observations of some of the reactions which have been proposed as intermediate steps in the oxidation of halide ions or reduction of halogens.

R SUPPLEMENTARY RESULTS

Sections R4, R5 and R13 contain experimental data and results which were not included in the corresponding discussion sections 4, 5, and 13. These supplementary sections contain certain experimental details and primary or untreated results, from which an assessment of the reliability of the conclusions made in the discussion sections can be made.

In evaluating the reliability of the data it should be noted that each decay curve and rate constant is the average of at least 4 separate oscilloscope traces. Where oscilloscope traces are shown to illustrate the accuracy of measurement or fit of a theoretical reaction scheme, only one of the set is shown. The reproducibility of the traces is always better than 10%.

SECTION R4 SUPPLEMENTARY RESULTS
RADIATION CHEMISTRY

R4.5 FORMATION OF Cl_2^- FROM OH

R4.5.3 Evaluation of equilibrium constants

To illustrate the precision of the results used to obtain equilibrium constants, Fig. R4.5A shows typical oscilloscope traces from which Cl_2^- yields were measured. Each D_∞/D point in Figure 4.5A is the average of at least 3 oscilloscope traces with reproducibility of better than 10%.

R4.7 DECAY OF Br_2^-

In deaerated neutral or acidified bromide solution the decay of Br_2^- can be described by some or all of the following equations.

	Rate constant ($\text{l mol}^{-1} \text{s}^{-1}$)	
(1) $\text{Br}_2^- + \text{Br}_2^- \longrightarrow \text{Br}_3^- + \text{Br}^-$	3.3×10^9	a
(2) $\text{Br}_2^- + \text{e}^- \text{aq} \longrightarrow 2\text{Br}^-$	-	
(3) $\text{e}^- \text{aq} + \text{e}^- \text{aq} \longrightarrow \text{H}_2 + 2\text{OH}^-$	5×10^9	b
(4) $\text{e}^- \text{aq} + \text{Br}_3^- \longrightarrow \text{Br}_2^- + \text{Br}^-$	2×10^9	c
(5) $\text{e}^- \text{aq} + \text{H}^+ \longrightarrow \text{H}$	2.3×10^{10}	b
(6) $\text{H} + \text{Br}_2^- \longrightarrow \text{H}^+ + 2\text{Br}^-$	-	
(7) $\text{H} + \text{H} \longrightarrow \text{H}_2$	1×10^{10}	b
(8) $\text{H} + \text{Br}_3^- \longrightarrow \text{H}^+ + \text{Br}_2^- + \text{Br}^-$	2×10^{10}	c

References:

- (a) Cercek, Ebert, Gilbert, and Swallow (1965)
- (b) Anlar and Neta (1967)
- (c) Estimated from rate constants of similar reactions given in ref (b).

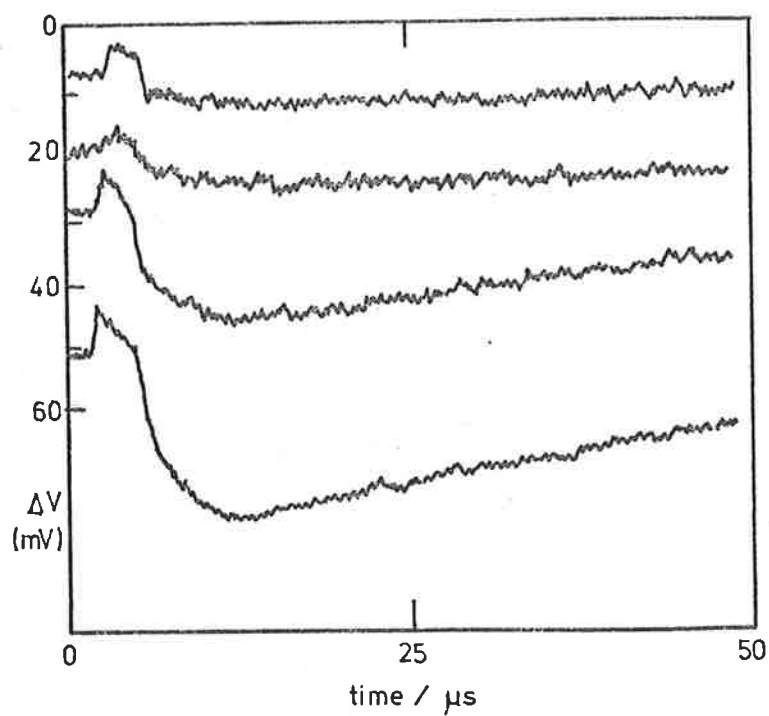


Fig.R4.5A

$$[Cl^-] = 2 \times 10^{-5} \text{ mol l}^{-1}$$

$$[H^+] = 0.07 \text{ mol l}^{-1}$$

$$0.14 \text{ mol l}^{-1}$$

$$0.40 \text{ mol l}^{-1}$$

$$0.70 \text{ mol l}^{-1}$$

$$\lambda = 365 \text{ nm}$$

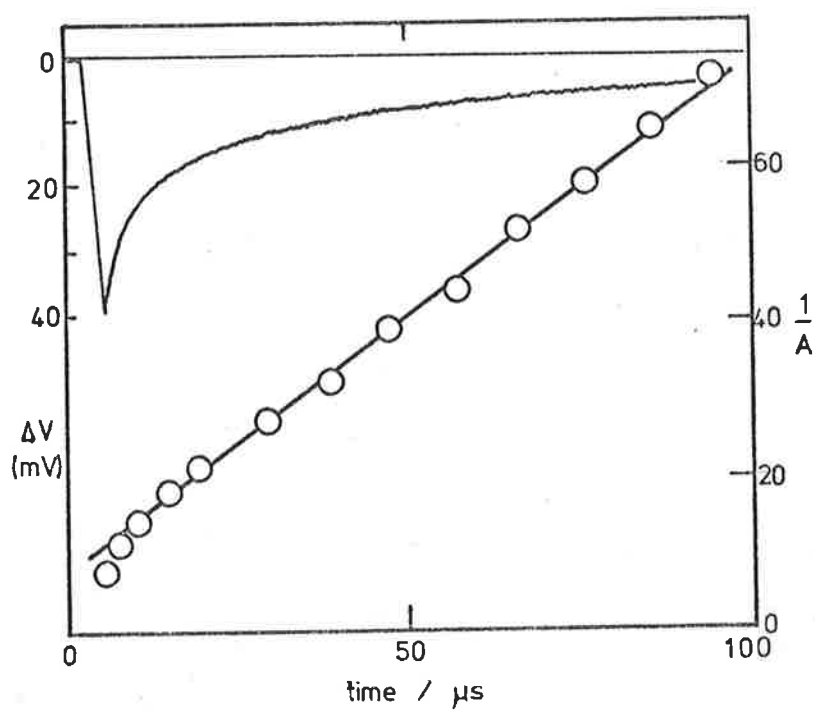


Fig.R4.7A

$$\lambda = 365 \text{ nm}$$

$$l = 1.0 \text{ cm}$$

$$2k = 5.1 \times 10^9$$

R4.7.1 Deaerated neutral bromide

Reactions (1) to (4) describe the decay of Br_2^- in deaerated neutral bromide. Fig. R4.7A shows a typical oscilloscope trace and experimental $1/\text{absorbance}$ against time points. From the variation of the apparent second order rate constant with time it can be estimated that $k_2 = 8 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

R4.7.2 Acidified deaerated bromide

Fig. R4.7B shows the decay of Br_2^- from a deaerated acid solution, in which reactions (1) and (5) to (6) are important. It can be estimated that $k_6 = 5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

R4.7.3 Nitrous oxide saturated bromide

The decay of Br_2^- in nitrous oxide saturated bromide solution is good second order with a best fit second order rate constant of $3.3 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ (see Fig. R4.7C).

R4.8 DECAY OF Cl_2^-

In deaerated neutral or acid chloride solution the following reactions may be important.

	Rate constant ($\text{l mol}^{-1} \text{ s}^{-1}$)	
(1) $\text{Cl}_2^- + \text{Cl}_2^- \longrightarrow \text{Cl}_3^- + \text{Cl}^-$	5.5×10^9	a
(2) $\text{Cl}_2^- + \text{e}^- \text{aq} \longrightarrow 2\text{Cl}^-$	-	
(3) $\text{e}^- \text{aq} + \text{e}^- \text{aq} \longrightarrow \text{H}_2 + 2\text{OH}^-$	5×10^9	b
(4) $\text{e}^- \text{aq} + \text{Cl}_3^- \longrightarrow \text{Cl}_2^- + \text{Cl}^-$	2×10^{10}	c
(5) $\text{e}^- \text{aq} + \text{H}^+ \longrightarrow \text{H}$	2.3×10^{10}	b
(6) $\text{H} + \text{Cl}_2^- \longrightarrow \text{H}^+ + 2\text{Cl}^-$	-	
(7) $\text{H} + \text{H} \longrightarrow \text{H}_2$	1×10^{10}	b
(8) $\text{H} + \text{Cl}_3^- \longrightarrow \text{H}^+ + \text{Cl}_2^- + \text{Cl}^-$	2×10^{10}	c

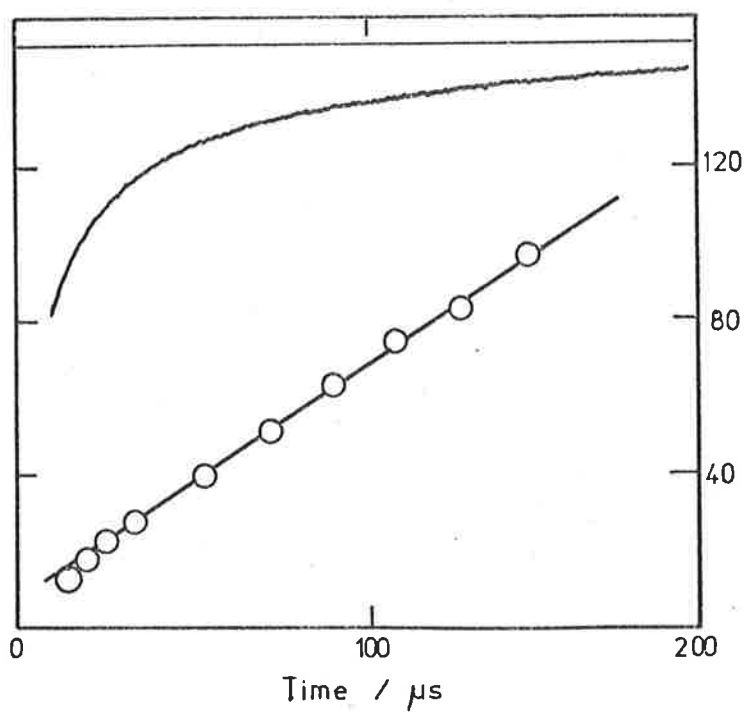


Fig.R4.7B

$\lambda = 365 \text{ nm}$
 $l = 1.0 \text{ cm}$
 $2k = 4.9 \times 10^9$

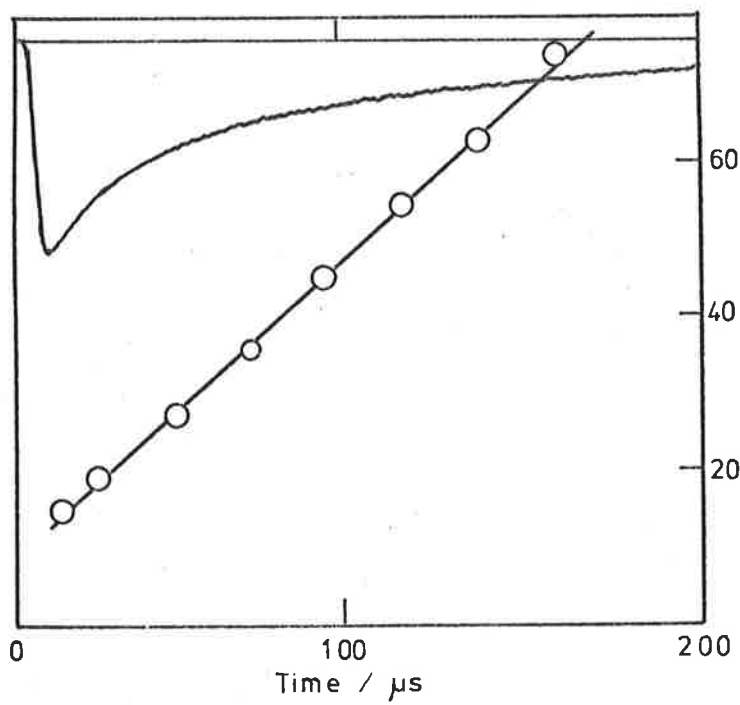


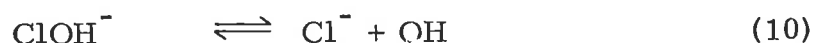
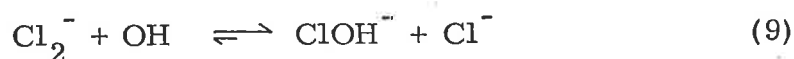
Fig.R4.7C

$\lambda = 365 \text{ nm}$
 $l = 1.0 \text{ cm}$
 $2k = 3.3 \times 10^9$

References:

- (a) This work (See Table 5.4A)
- (b) Anbar and Neta (1967)
- (c) Estimated from rate constants of similar reactions given in ref. (b)

If spur reactions are important and Cl_2^- is formed in excess of equilibrium bulk concentrations the re-establishment of equilibrium with ClOH^- or OH^- may be an important process in the decay of Cl_2^- (see 4.5)

R4.8.1 Deaerated neutral chloride

The decay of Cl_2^- in neutral deaerated solution is illustrated in Fig. R4.8A. The initial rapid decay is due to reaction (2) with a rate constant of $1 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. At longer times the decay which was previously adequately described by reactions (1) to (4) approaches first order as reactions (9) and (10) become more important.

R4.8.2 Acidified deaerated chloride solutions

Reactions (1) and (5) to (8) describe the decay of Cl_2^- in acidic deaerated solution. The second order decay illustrated in Fig. R4.8B shows initial curvature due to reaction (6) with a rate constant of $1 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$.

R4.8.3 Nitrous oxide saturated chloride solution

At pH 4 and 0.5 mol l^{-1} chloride, nitrous oxide increases the yield of Cl_2^- from $5.2 \times 10^{-6} \text{ mol l}^{-1}$ to $10.1 \times 10^{-6} \text{ mol l}^{-1}$ for a dose of about 2000 rads. The expected doubling of yield is observed (see 4.3.2), indicative of complete radical scavenging.

The decay of Cl_2^- under these conditions is good second order as shown in Fig. R4.8C with a rate constant of $6.0 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

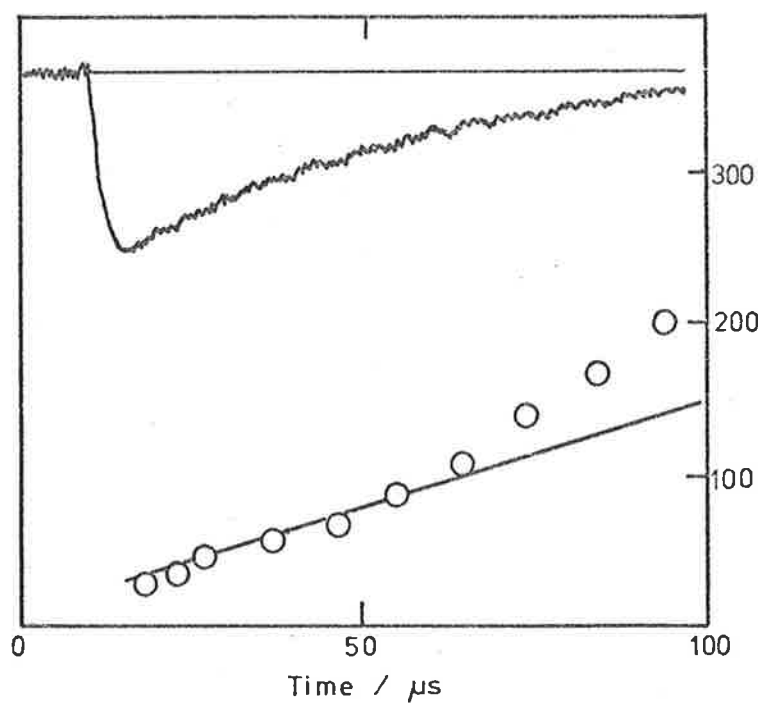


Fig. R4.8A

$\lambda = 350 \text{ nm}$
 $l = 1.0 \text{ cm}$
 $2k = 1.5 \times 10^{10}$

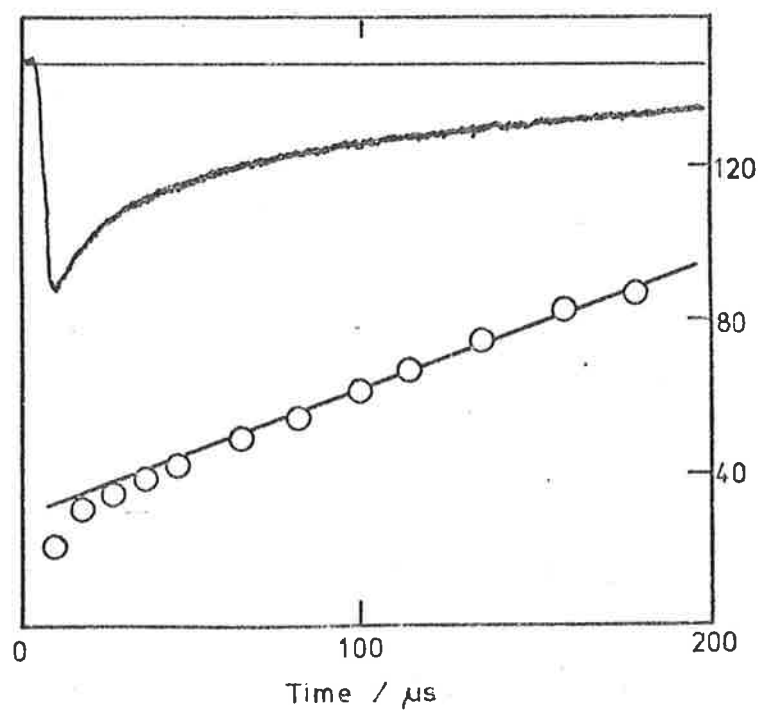


Fig. R4.8B

$\lambda = 350 \text{ nm}$
 $l = 1.0 \text{ cm}$
 $2k = 6.5 \times 10^9$

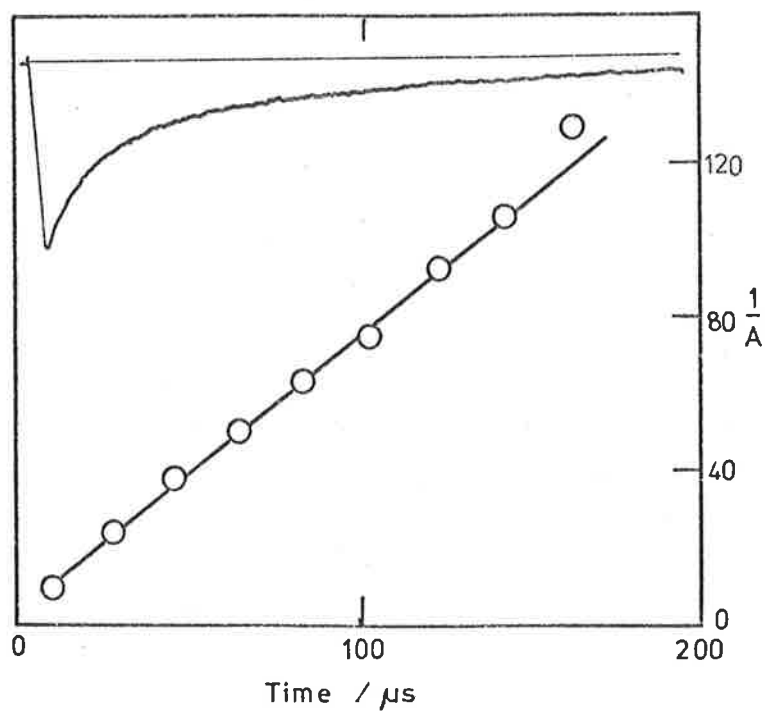


Fig.R4.8C

$\lambda = 350 \text{ nm}$

$l = 1.0 \text{ cm}$

$2k = 6.0 \times 10^9$

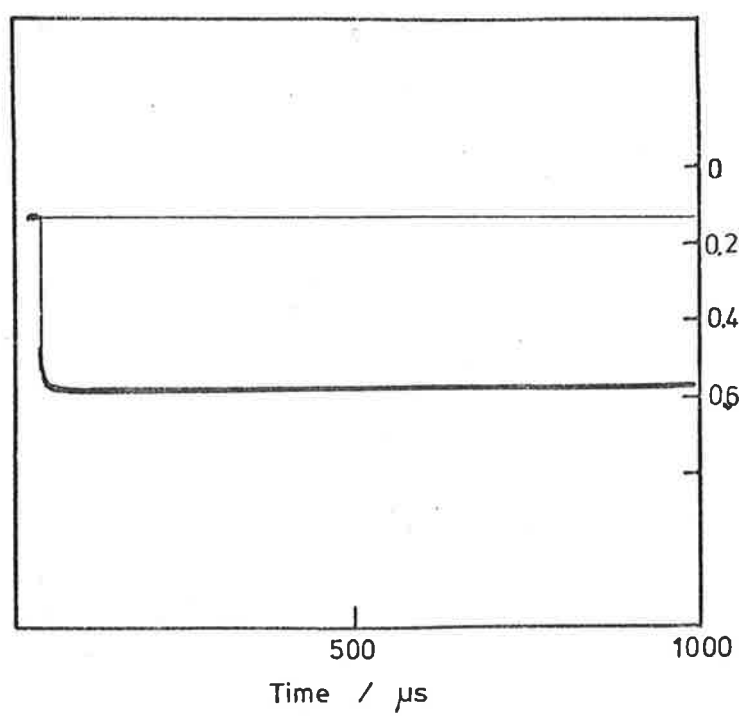


Fig.R4.9A

$\lambda = 365 \text{ nm}$

$l = 1.0 \text{ cm}$

R5.

R4.9 DECAY OF I_2^-

R4.9.1 Nitrous oxide saturated iodide solution

A dose of approximately 2500 rads produces an I_2^- concentration of $12.4 \times 10^{-6} \text{ mol l}^{-1}$ from nitrous oxide saturated iodide solution, compared to a yield of $6.1 \times 10^{-6} \text{ mol l}^{-1}$ from the same solution without nitrous oxide.

Fig. R4.9A shows the pulse radiolysis of this system at 335 nm where $\epsilon_{I_2^-} = \frac{1}{2} \epsilon_{I_3^-}$. The expected 2:1 stoichiometry is observed.

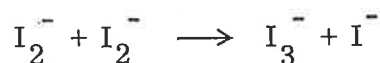


Fig. R4.9B shows the same solution at 405 nm where the decay of I_2^- is good second order with a rate constant of $8.0 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

Fig. R4.9C shows the same solution at 313 nm where the formation of I_3^- is good second order with a rate constant of $7.4 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

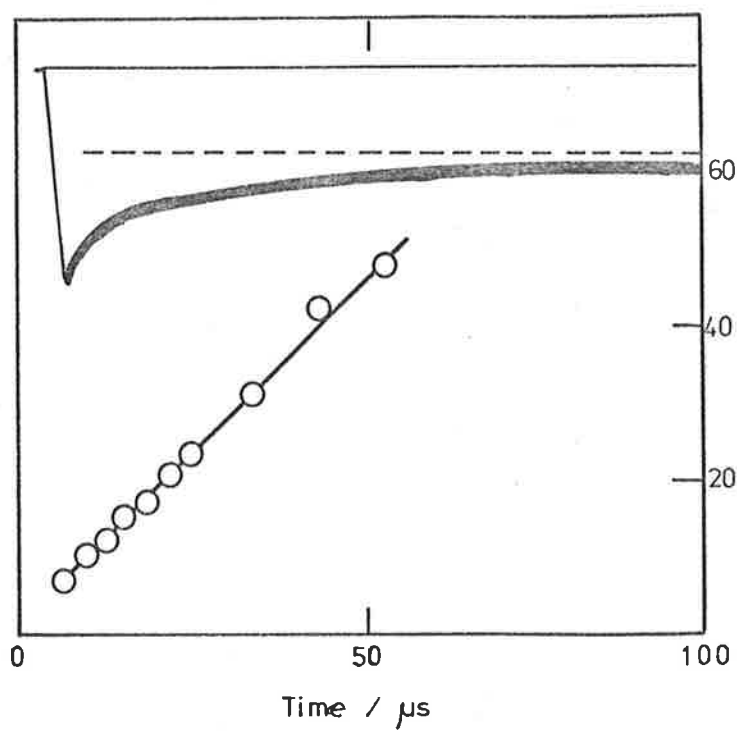


Fig.R4.9B

$\lambda = 405 \text{ nm}$
 $l = 1.0 \text{ cm}$
 $2k = 7.5 \times 10^9$

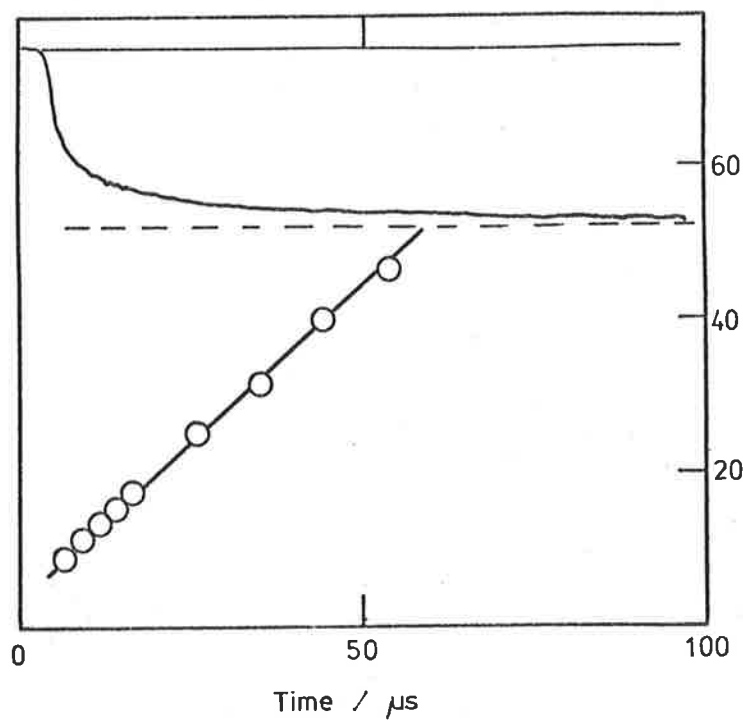


Fig.R4.9C

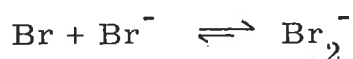
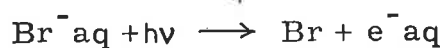
$\lambda = 313 \text{ nm}$
 $l = 1.0 \text{ cm}$
 $2k = 7.8 \times 10^9$

SECTION R5 SUPPLEMENTARY RESULTS

FLASH PHOTOLYSIS

R5.3 DECAY OF Br_2^-

In neutral and acidified bromide solution a general reaction scheme can be written using values of rate constants reported in the literature.



Rate constant ($\text{l mol}^{-1} \text{s}^{-1}$)		
(1) $\text{Br}_2^- + \text{Br}_2^- \longrightarrow \text{Br}_3^- + \text{Br}^-$	3.3×10^9	a
(2) $\text{Br}_2^- + \text{e}^-_{\text{aq}} \longrightarrow 2\text{Br}^-$	-	
(3) $\text{e}^-_{\text{aq}} + \text{e}^-_{\text{aq}} \longrightarrow \text{H}_2 + 2\text{OH}^-$	5×10^9	b
(4) $\text{e}^-_{\text{aq}} + \text{H}_2\text{O} \longrightarrow \text{H} + \text{OH}^-$	18	b
(5) $\text{e}^-_{\text{aq}} + \text{Br}_3^- \longrightarrow \text{Br}_2^- + \text{Br}^-$	2×10^{10}	c
(6) $\text{e}^-_{\text{aq}} + \text{H}^+ \longrightarrow \text{H}$	23×10^{10}	b
(7) $\text{Br}_2^- + \text{H} \longrightarrow \text{H}^+ + 2\text{Br}^-$	-	
(8) $\text{H} + \text{H} \longrightarrow \text{H}_2$	1×10^{10}	b
(9) $\text{H} + \text{Br}_3^- \longrightarrow \text{H}^+ + \text{Br}_2^- + \text{Br}^-$	2×10^{10}	c
(10) $\text{e}^-_{\text{aq}} + \text{O}_2 \longrightarrow \text{O}_2^-$	2×10^{10}	b
(11) $\text{O}_2^- + \text{Br}_2^- \longrightarrow \text{O}_2 + 2\text{Br}^-$	-	
(12) $\text{O}_2^- + \text{Br}_3^- \longrightarrow \text{O}_2 + \text{Br}^- + \text{Br}_2^-$	1×10^9	a
(13) $\text{H} + \text{O}_2 \longrightarrow \text{HO}_2$	2×10^{10}	b
(14) $\text{HO}_2 + \text{Br}_2^- \longrightarrow \text{O}_2 + \text{H}^+ + 2\text{Br}^-$	-	
(15) $\text{HO}_2 + \text{Br}_3^- \longrightarrow \text{H}^+ + \text{Br}^- + \text{Br}_2^- + \text{O}_2$	1.5×10^8	a
(16) $\text{HO}_2 + \text{HO}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$	7.6×10^5	d

References:

- (a) Cercek, Ebert, Gilbert and Swallow (1965)
- (b) Anbar and Neta (1967)
- (c) Estimated from rate constants of similar reactions given in ref. (b)
- (d) Behar, Czapski, Rabani, Dorfman and Schwarz (1970)

The data were generally treated by computer fitting the appropriate reaction scheme to the observed decay curve using the known rate constants and estimating the unknown one.

R5.3.1 Deaerated neutral bromide solution

Decay of Br_2^- is described by reactions (1) - (5). Fig. R5.3A shows a typical oscilloscope trace, second order curve using $k_2 = 1.0 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$.

R5.3.2 Aerated neutral bromide solutions

The reaction scheme is reactions (1) and (10) - (12). Fig. R5.3B shows the oscilloscope trace and fit of the second order points by the computer simulated absorbances using $k_{11} = 6 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

R5.3.3 Acidified deaerated bromide solution

Br_2^- decay is described by reactions (1) and (6) to (9). With $k_7 = 7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ the computer fit illustrated in Fig. R5.3C is obtained.

R5.3.4 Acidified aerated bromide solution

Fig. R5.3D shows an oscilloscope trace, experimental $1/\text{absorbance}$ against time points and a theoretical computer simulated $1/\text{absorbance}$ against time curve using reactions (1) and (13) - (16) with $k_{14} = 4 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

R5.3.5 Nitrous oxide saturated bromide solution

The decay of Br_2^- in neutral nitrous oxide saturated bromide solution is good second order as shown by the linearity of $1/\text{absorbance}$

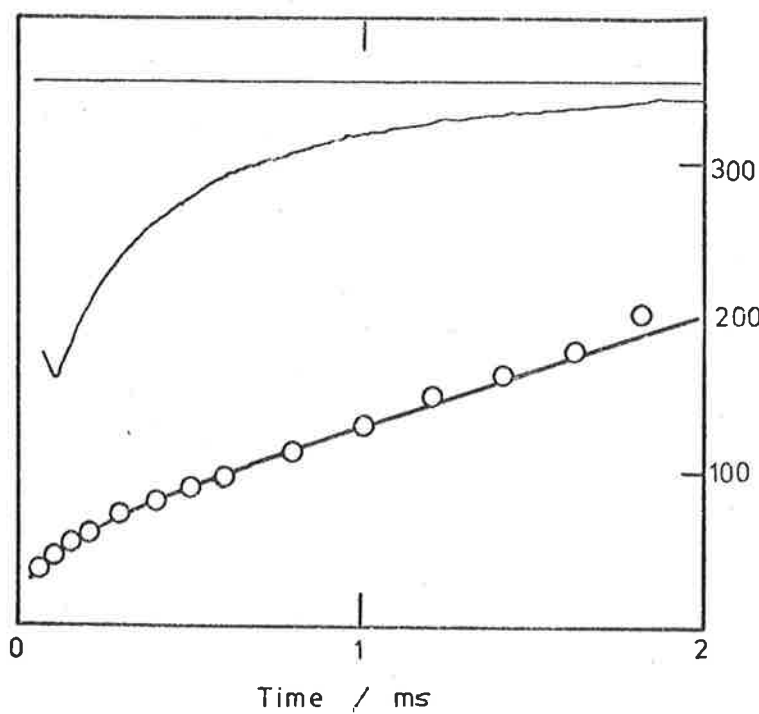


Fig.R5.3A

$\lambda = 366 \text{ nm}$
 $l = 10 \text{ cm}$

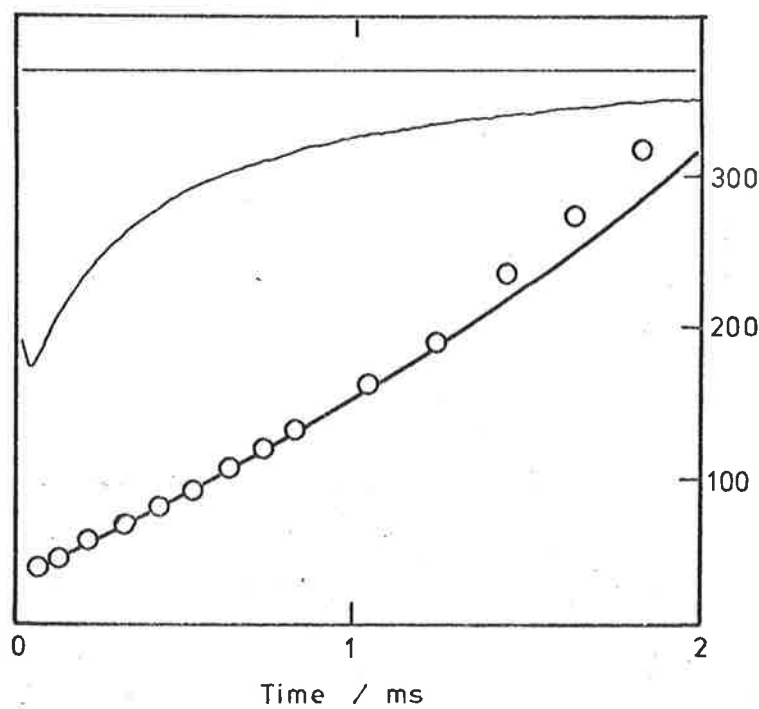


Fig.R5.3B

$\lambda = 366 \text{ nm}$
 $l = 10 \text{ cm}$

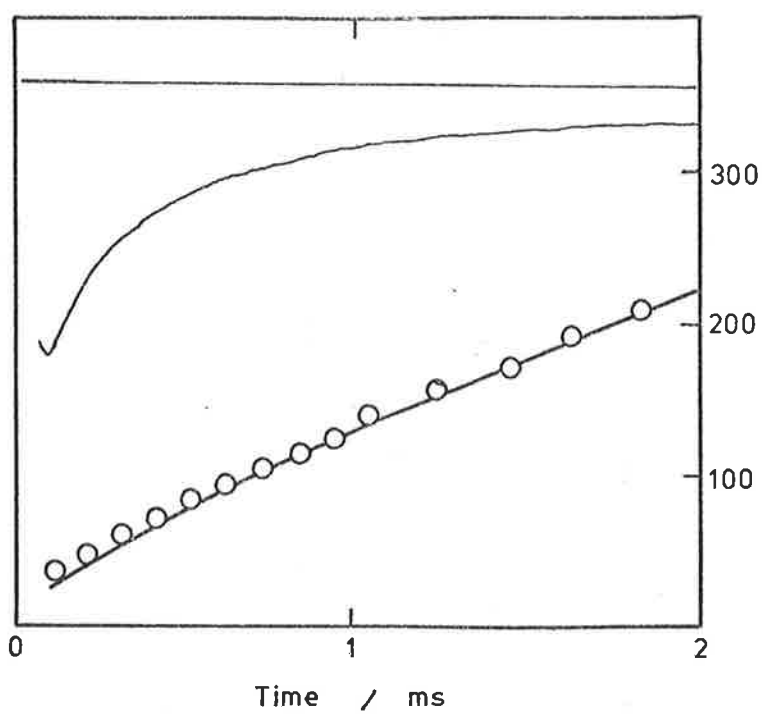


Fig.R5.3C

$\lambda = 366 \text{ nm}$
 $l = 10 \text{ cm}$

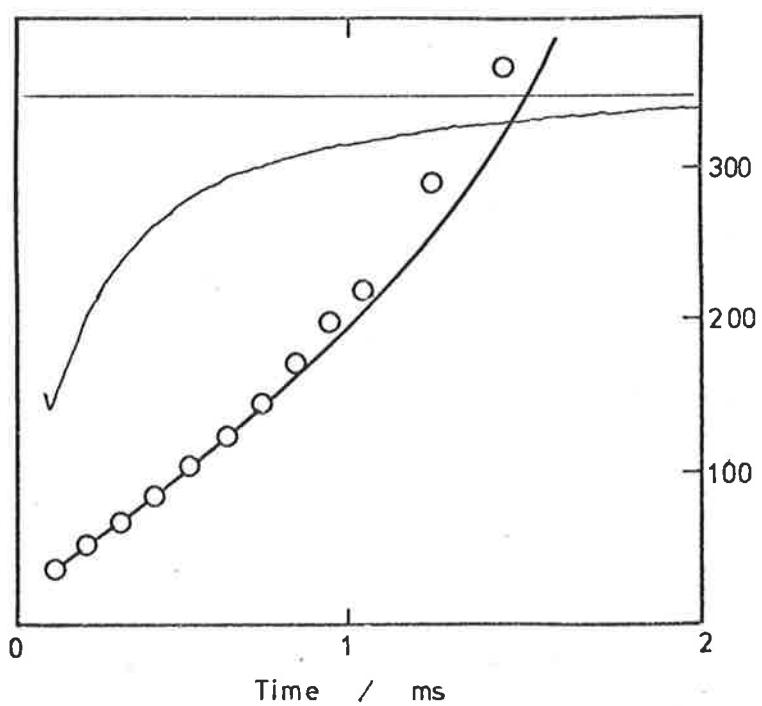


Fig.R5.3D

$\lambda = 366 \text{ nm}$
 $l = 10 \text{ cm}$

R8.

against time curves (For example see Fig. R5.3E). The second order rate constant varies as the bromide concentration is changed (See Table 5.3B). This variation can be attributed to the effect of ionic strength on the rate. Fig. R5.3F is a plot of $\log_{10}(2k)$ against the function $\frac{1.18\sqrt{I}}{1 + 1.32\sqrt{I}}$ which assumes a distance of closest approach of 4 Å in the Bronsted, Bjerrum and Christiansen equation for the variation of activities with ionic strength. Within the limits of experimental error the plot is linear and shows a slope of +1 expected for reaction between two univalent negative ions.

R5.3.5 Neutral aqueous bromine solution

Fig. R5.3G shows a typical oscilloscope trace and best fit first order rate curve produced by flash photolysis of neutral aqueous bromine solution. The transient absorbance is only about 25% of that in a bromine solution containing bromide and acid, and the decay of Br_2^- is neither good first nor second order.

R5.3.7 Acidified bromine/bromide solution

Decay of the $10\ \mu\text{mol l}^{-1}$ concentrations of Br_2^- produced by flash photolysis of acidified bromine/bromide solution exhibits good second order rate kinetics (See Fig. R5.3H). The rate constant at 25°C is $(5.3 \pm 0.5) \times 10^9\ \text{l mol}^{-1}\text{s}^{-1}$.

R5.3.8 Hydrogen peroxide/bromide solution

Flash photolysis of $10^{-3}\ \text{mol l}^{-1}$ hydrogen peroxide solutions containing bromide and acid produces large ($10\ \mu\text{mol l}^{-1}$) concentrations of Br_2^- decaying by good second order kinetics with a rate constant of $(5.5 \pm 0.8) \times 10^9\ \text{l mol}^{-1}\text{s}^{-1}$ (See Fig. R5.3I)

Higher H_2O_2 concentrations produce lower effective Br_2^- concentrations (see 5.1.3). As $[\text{H}_2\text{C}_2\text{O}_4]$ increases to $0.1\ \text{mol l}^{-1}$ the second order fit deteriorates and a first order component becomes

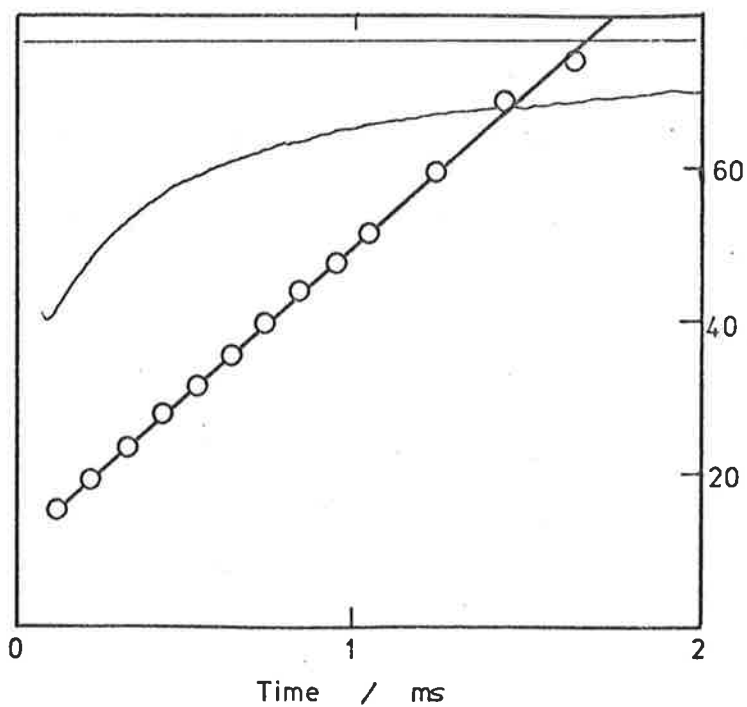


Fig. R5.3E

$\lambda = 366 \text{ nm}$

$l = 10 \text{ cm}$

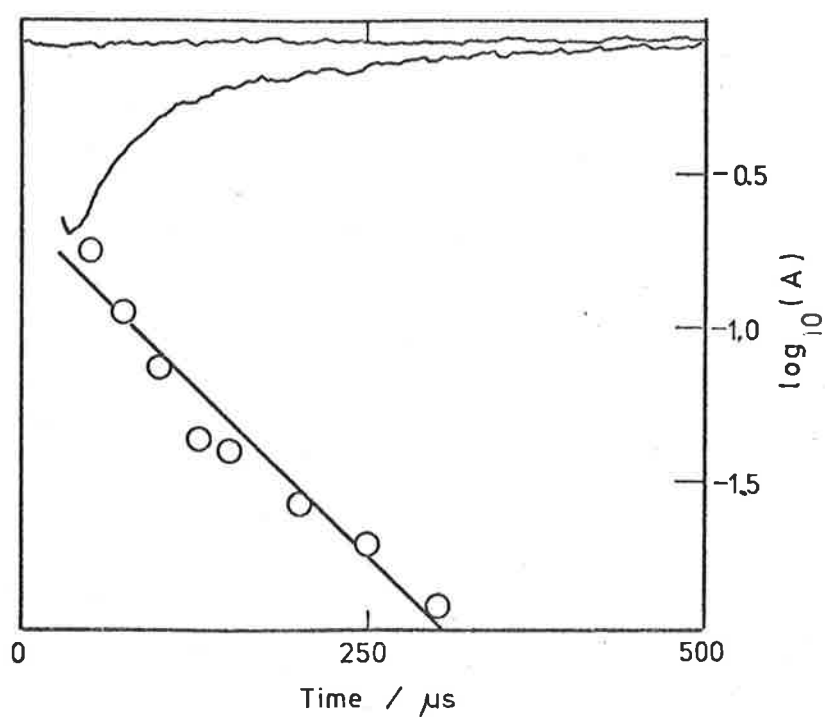


Fig. R5.3G

$\lambda = 366 \text{ nm}$

$l = 10 \text{ cm}$

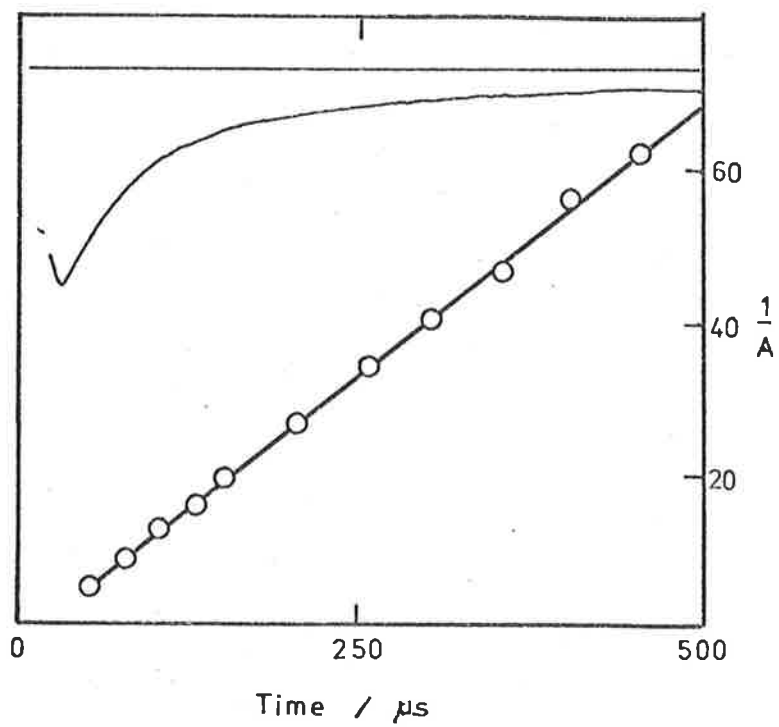


Fig.R5.3H

$$\lambda = 366 \text{ nm}$$

$$l = 5.0 \text{ cm}$$

$$2k = 5.3 \times 10^9$$

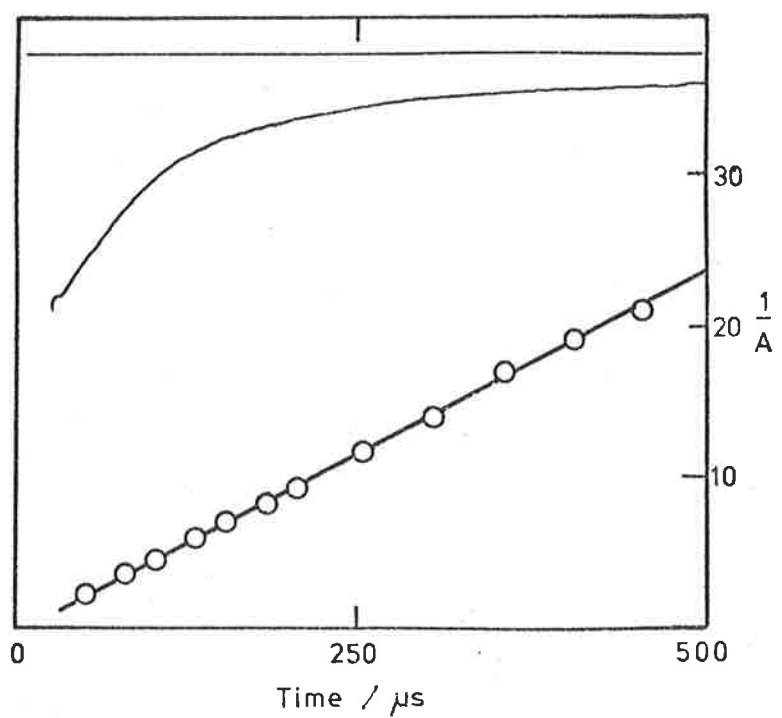


Fig.R5.3I

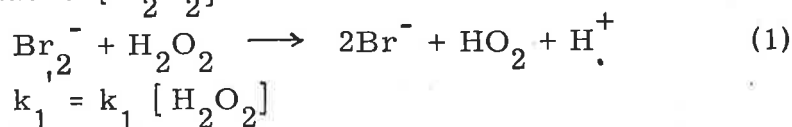
$$\lambda = 366 \text{ nm}$$

$$l = 10 \text{ cm}$$

$$2k = 5.5 \times 10^9$$

R9.

apparent. The decay can be analyzed as competing first and second order reactions where the pseudo first order rate constant, k_1' , is proportional to $[H_2O_2]$



The absolute second order rate constant, k_1 is about $(1.5 \pm 0.5) \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ (see Table R5.3B).

Table R5.3B

$[H_2O_2]$ (mol l^{-1})	k_1' (s^{-1})	k_1 ($\text{l mol}^{-1} \text{ s}^{-1}$)
10^{-2}	5×10^3	-
5×10^{-2}	$(9 \pm 3) \times 10^3$	$(1.8 \pm 0.6) \times 10^5$
10^{-1}	$(13 \pm 3) \times 10^3$	$(1.5 \pm 0.5) \times 10^5$
Average		$(1.5 \pm 0.5) \times 10^5$

R5.3.9 Acidified ferric bromide solution produces Br_2^- which decays by a good second order process with rate constant of $(5.2 \pm 0.8) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ at 25°C (See Fig. R5.3J). Small semipermanent ($t_{1/2} \sim 1 \text{ min}$) changes are produced in the solution due to removal of $FeBr^{2+}$ which has an extinction coefficient of about 500 at 366nm.

R5.3.10 Temperature dependence of Br_2^- disproportionation rate constant

Acidified bromine/bromide solutions were photolysed to produce Br_2^- (See R5.3.7). The bimolecular rate constants ($2k$) are listed as a function of temperature in Table R5.3C.

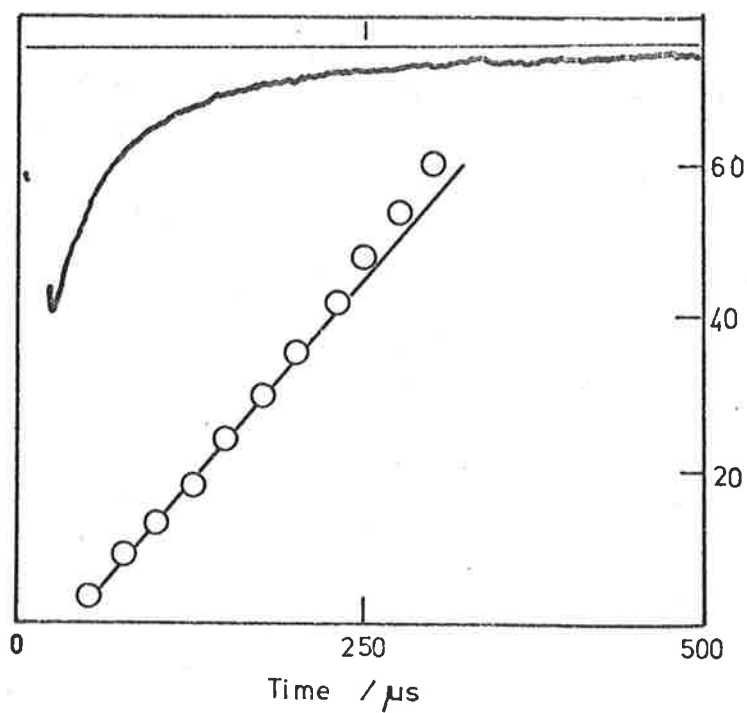


Fig. R5.3J

$\lambda = 366 \text{ nm}$

$l = 5.0 \text{ cm}$

$2k = 5.4 \times 10^9$

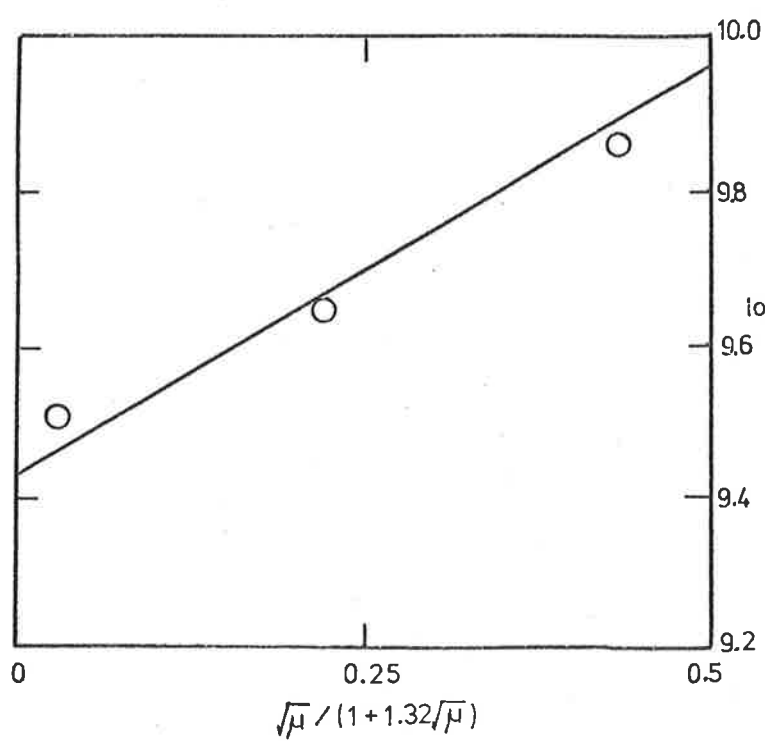


Fig. R5.3F

Effect of Ionic

Strength on

$\frac{2k}{\text{Br}_2^- + \text{Br}_2^-}$

Table R5.3C

Temp (°C)	$2k (\text{Br}_2^- + \text{Br}_2^-)$ ($\text{l mol}^{-1} \text{s}^{-1}$)
15.4	4.5×10^9
24.8	5.15×10^9
30.8	5.6×10^9
38.7	6.4×10^9

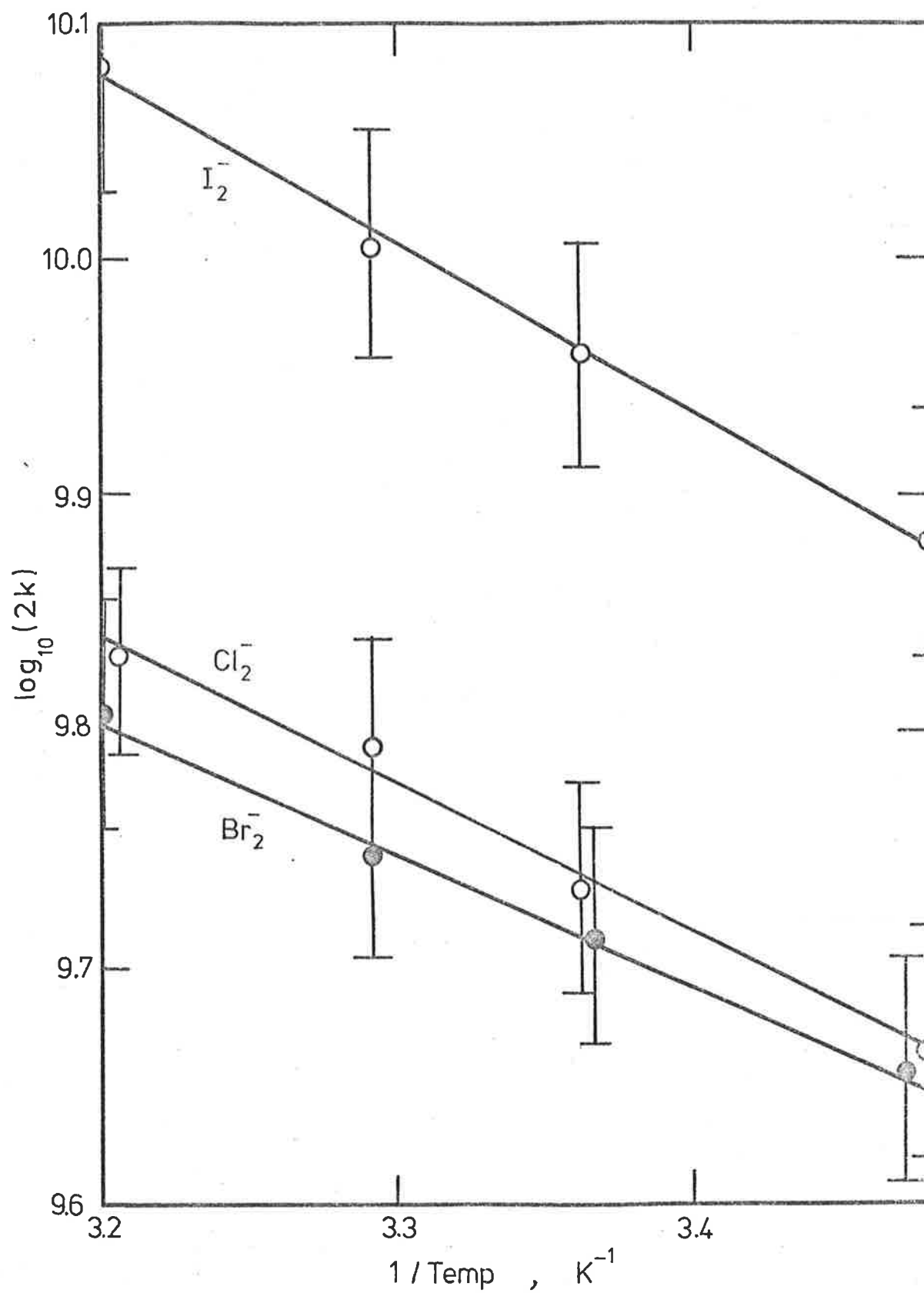
Figure R5.3K shows the Arrhenius plot of these data, from which the parameters in 5.3.10 were obtained.

R5.4 DECAY OF Cl_2^-

In neutral and acidified chloride solution a general reaction scheme can be constructed using values of rate constants in the literature or estimating values by comparison with analogous bromide or chloride systems.

	Rate constant ($\text{l mol}^{-1} \text{s}^{-1}$)	
(1) $\text{Cl}_2^- + \text{Cl}_2^- \longrightarrow \text{Cl}_3^- + \text{Cl}^-$	5.5×10^9	a
(2) $\text{Cl}_2^- + \text{e}^- \text{aq} \longrightarrow 2\text{Cl}^-$	-	
(3) $\text{e}^- \text{aq} + \text{e}^- \text{aq} \longrightarrow \text{H}_2 + 2\text{OH}^-$	5×10^9	b
(4) $\text{e}^- \text{aq} + \text{H}_2\text{O} \longrightarrow \text{H} + \text{OH}^-$	18	b
(5) $\text{e}^- \text{aq} + \text{Cl}_3^- \longrightarrow \text{Cl}_2^- + \text{Cl}^-$	2×10^{10}	c
(6) $\text{e}^- \text{aq} + \text{H}^+ \longrightarrow \text{H}$	2.3×10^{10}	b
(7) $\text{Cl}_2^- + \text{H} \longrightarrow \text{H}^+ + 2\text{Cl}^-$	-	
(8) $\text{H} + \text{H} \longrightarrow \text{H}_2$	1×10^{10}	b
(9) $\text{H} + \text{Cl}_3^- \longrightarrow \text{H}^+ + \text{Cl}_2^- + \text{Cl}^-$	2×10^{10}	c
(10) $\text{e}^- \text{aq} + \text{O}_2 \longrightarrow \text{O}_2^-$	2×10^{10}	b

Fig. R5.3K Arrhenius Plots $X_2^- + X_2^-$



R11.

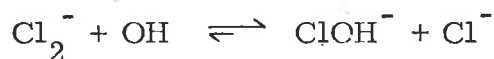
(11) $\text{O}_2^- + \text{Cl}_2^- \longrightarrow \text{O}_2 + 2\text{Cl}^-$	-	
(12) $\text{O}_2^- + \text{Cl}_3^- \longrightarrow \text{O}_2 + \text{Br}^- + \text{Br}_2^-$	10^9	c
(13) $\text{H} + \text{O}_2 \longrightarrow \text{HO}_2$	2×10^{10}	b
(14) $\text{HO}_2 + \text{Cl}_2^- \longrightarrow \text{O}_2 + \text{H}^+ + 2\text{Cl}^-$	-	
(15) $\text{HO}_2 + \text{Cl}_3^- \longrightarrow \text{H}^+ + \text{Cl}^- + \text{Cl}_2^- + \text{O}_2$	10^8	c
(16) $\text{HO}_2 + \text{HO}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$	7.6×10^5	d

References;

- (a) This work.
- (b) Anbar and Neta (1967)
- (c) Estimated by analogy with Br and/or I system
- (d) Behar, Czapski, Rabani, Dorfman & Schwarz (1970)

R5.4.1 Neutral deaerated chloride solution

Fig. R5.4A shows typical oscilloscope trace and first order decay plot for Cl_2^- produced by flash photolysis of dilute neutral chloride. The approximate first order rate constant is $1.5 \times 10^3 \text{ s}^{-1}$. The first order kinetics ~~is~~^{are} presumably due to the re-equilibration of Cl_2^- with ClOH^- and OH^- through;



At 0.5 mol l^{-1} chloride the decay of Cl_2^- approaches second order, with initial curvature. The decay curve was computer simulated using reactions (1) to (5) with $k_2 = 1.5 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. Fig. R5.4B shows the second order decay curve and a typical oscilloscope trace.

R5.4.2 Neutral aerated chloride solutions

Fig. R5.4C shows a typical oscilloscope trace and corresponding experimental and simulated second order plots of Cl_2^- decay in aerated neutral chloride. From reactions (1) and (10) - (12) a value of $k_{11} = 1.2 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ gave the most satisfactory fit.

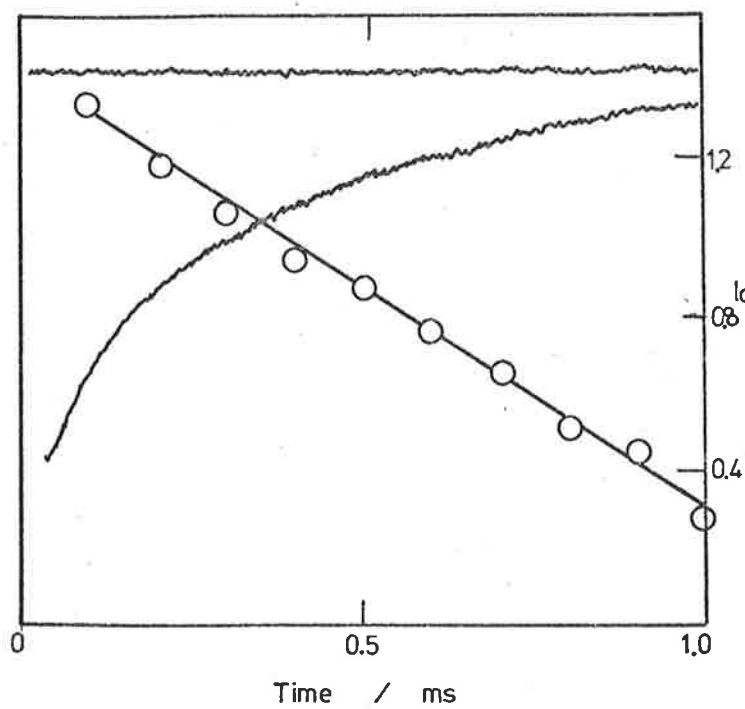


Fig. R5.4A

$\lambda = 366 \text{ nm}$

$l = 10 \text{ cm}$

$k = 2.5 \times 10^3 \text{ s}^{-1}$

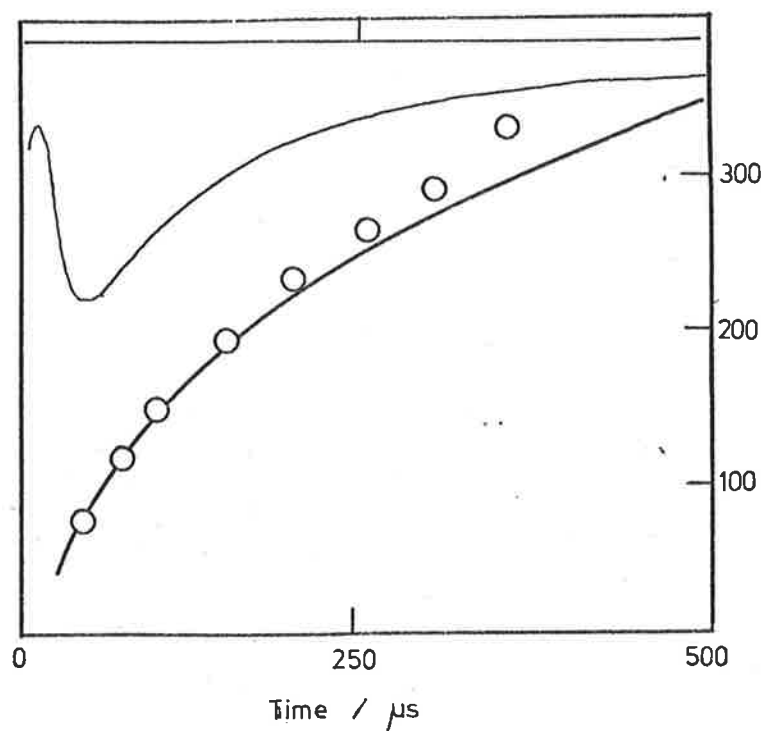


Fig. R5.4B

$\lambda = 366 \text{ nm}$

$l = 10 \text{ cm}$

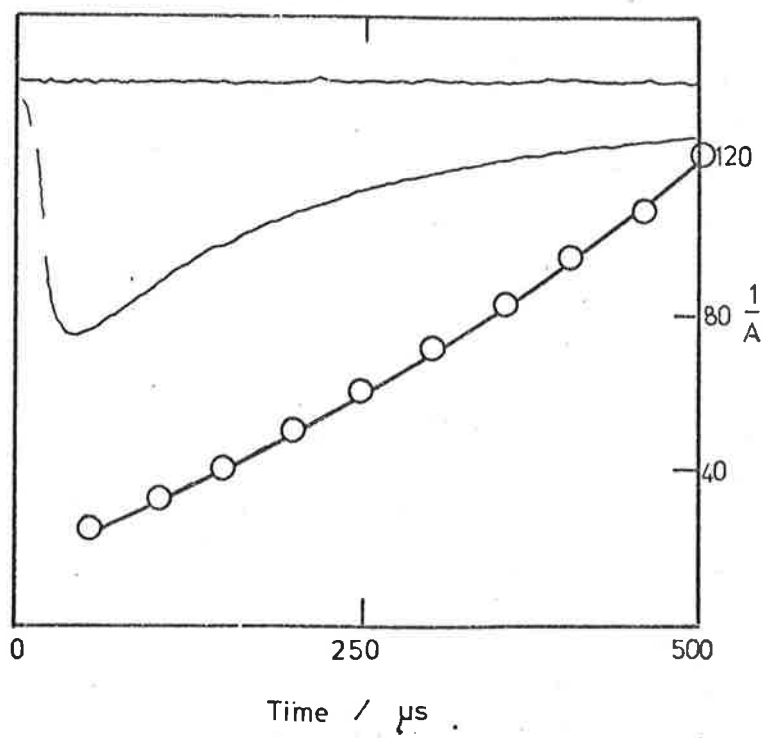


Fig. R5.4C

$\lambda = 366 \text{ nm}$
 $l = 10 \text{ cm}$

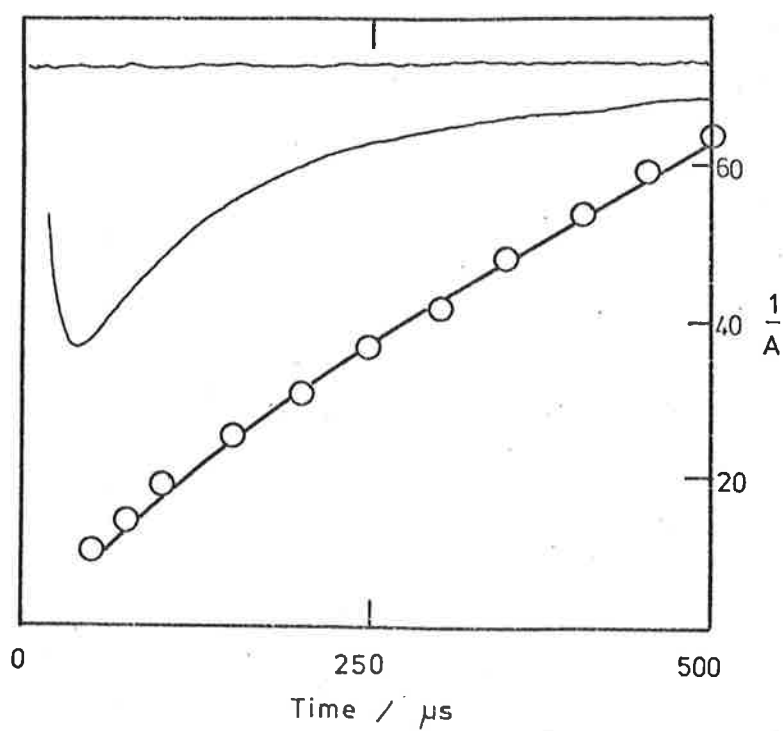


Fig. R5.4D

$\lambda = 366 \text{ nm}$
 $l = 10 \text{ cm}$

R5.4.3 Acidified deaerated chloride solution

Decay of Cl_2^- is described by reaction (1) and (6) to (9). Fig. R5.4D shows a typical oscilloscope trace, second order $1/\text{absorbance}$ against time points and the computed second order curve using $k_7 = 1 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$.

R5.4.4 Acidified aerated chloride solution

Reactions (1) and (13) to (16) describe the decay of Cl_2^- in acidified aerated chloride solution. Fig. R5.4E shows a typical oscilloscope trace and the experimental $1/\text{absorbance}$ against time points. The solid line is the computer simulated $1/\text{absorbance}$ against time curve using $k_{14} = 5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

R5.4.5 Nitrous oxide saturated chloride solutions

In dilute ($10^{-2} - 10^{-3} \text{ mol l}^{-1}$) chloride solutions at pH above 4 the decay of Cl_2^- approaches first order as illustrated by Fig. R5.4F which shows a typical oscilloscope trace and corresponding first order decay plot, due to re-equilibration (see R5.4.1, 5.4.1)

At pH 4 with 0.5 mol l^{-1} chloride, the Cl_2^- yield is doubled and the decay becomes good second order due to;

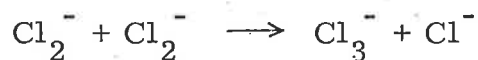


Fig. R5.4G shows the oscilloscope trace and second order rate constant is $(7 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

R5.4.6 Neutral aqueous chlorine solution

Fig. R5.4H shows an oscilloscope trace produced on flash photolysis of neutral chlorine and the corresponding first order $\log_{10}$ (absorbance) against time plot. The decay is rapid but not good first order. No kinetic measurements were made.

R5.4.7 Acidified chlorine/chloride solution

The decay of Cl_2^- from acidified chlorine solution is good second order (See Fig. R5.4I). The derived second rate constant is

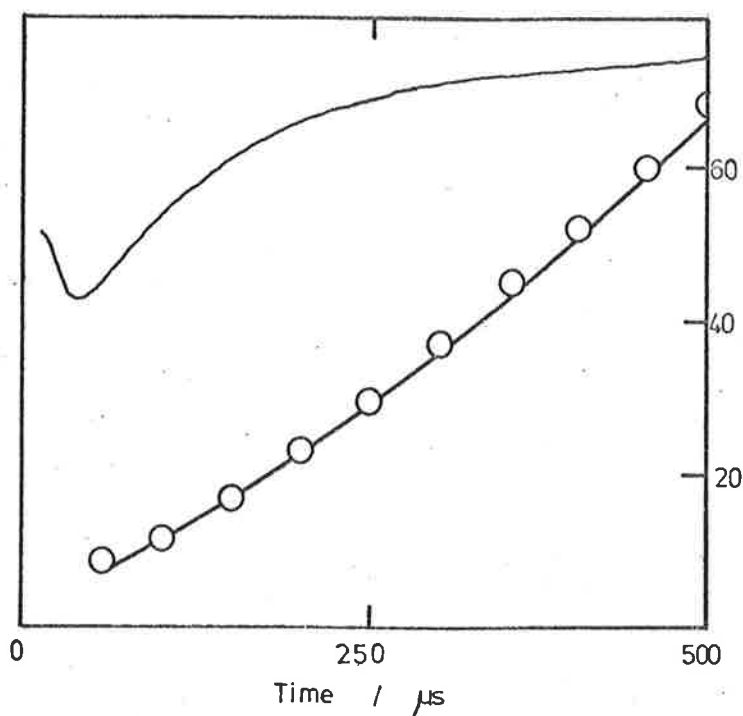


Fig. R5.4E

$\lambda = 366 \text{ nm}$

$l = 10 \text{ cm}$

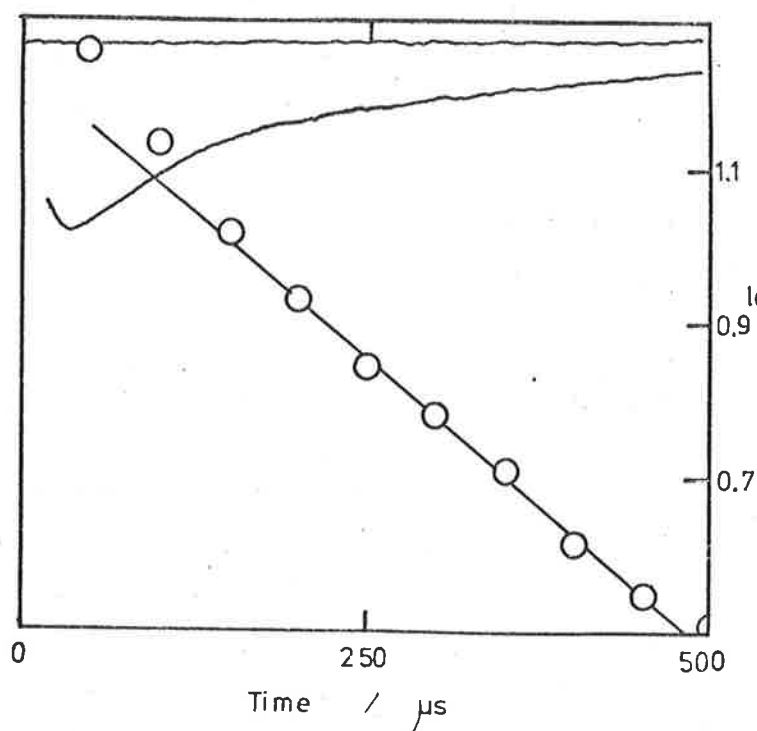


Fig. R5.4F

$\log_{10}(I_0^3/A)$

$\lambda = 366 \text{ nm}$

$l = 10 \text{ cm}$

$k = 3 \times 10^3 \text{ s}^{-1}$

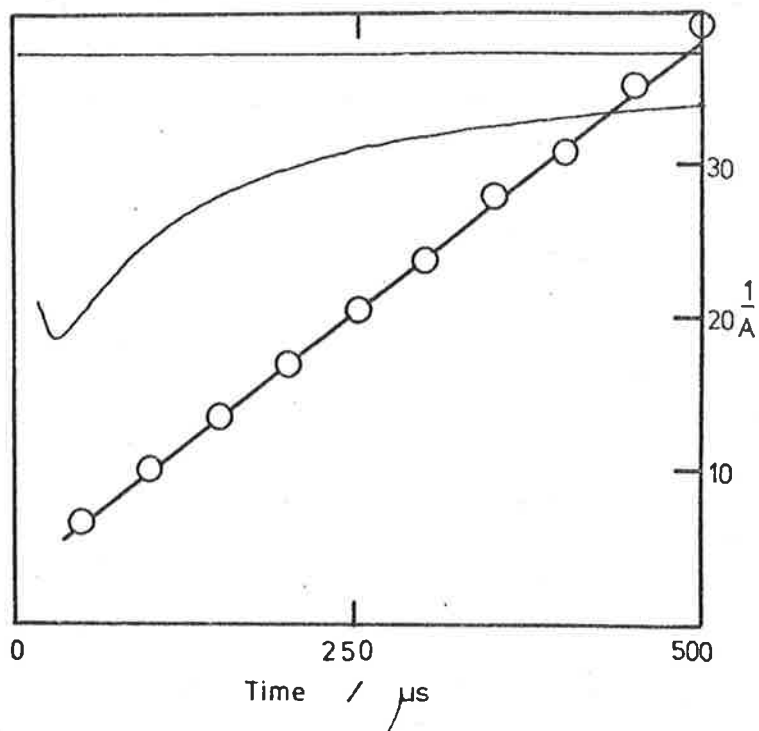


Fig. R5.4G

$\lambda = 366 \text{ nm}$
 $l = 10 \text{ cm}$
 $2k = 7.0 \times 10^9$

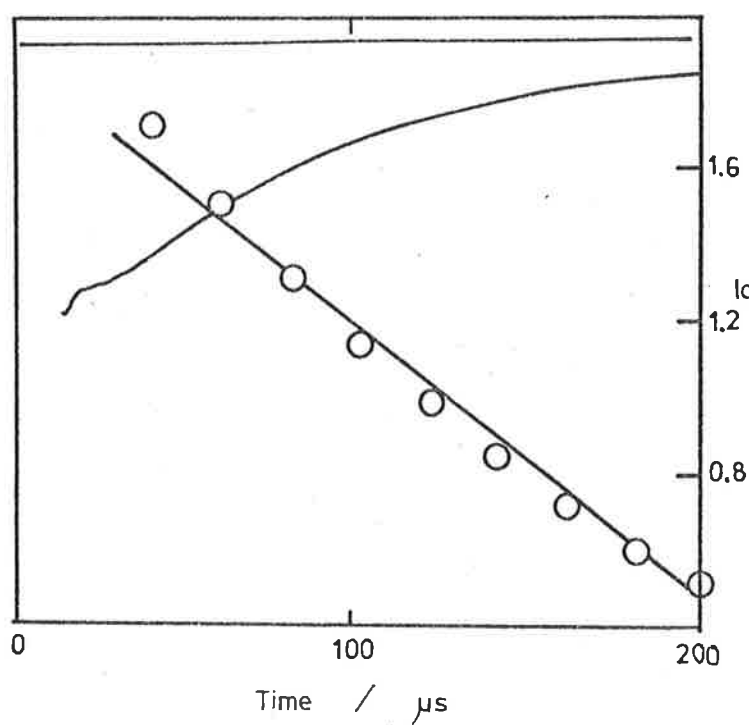


Fig. R5.4H

$\lambda = 366 \text{ nm}$
 $l = 10 \text{ cm}$
 $k = 5.3 \times 10^3 \text{ s}^{-1}$

R13.

$$(5.5 \pm 0.5) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}.$$

R5.4.8. Acidified hydrogen peroxide /chloride solution

Fig. R5.4J illustrates the good second order decay of Cl_2^- from acidified dilute hydrogen peroxide/chloride solution. The second order rate constant is $(5.5 \pm 1) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

With $10^{-1} \text{ mol l}^{-1}$ hydrogen peroxide the rate of decay of Cl_2^- was increased significantly and the decay approached first order, with a rate constant of $2 \times 10^4 \text{ s}^{-1}$.

R5.4.9 Acidified ferric chloride solution

Cl_2^- produced from $\text{FeCl}^{2+}_{\text{aq}}$ decays by a good second order process initially but tails off towards first order after 2 half lives. This apparent first order component arises because of absorbance of $\text{FeCl}^{3+}_{\text{aq}}$ at the wavelength of observation. By computer simulation the experimental $1/\text{absorbance}$ against time curve can be fitted with a simple second order Cl_2^- decay rate constant $(5.5 \pm 0.8) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. (See Fig. R5.4K).

R5.4.10 Temperature dependence of Cl_2^- disproportionation rate constant

The temperature dependence of the Cl_2^- disproportionation rate constant is shown in Table R5.4B.

Table R5.4B

Temp °C	$2k (\text{Cl}_2^- + \text{Cl}_2^-)$ ($\text{l mol}^{-1} \text{s}^{-1}$)
14.2	4.6×10^9
23.9	5.4×10^9
30.9	6.2×10^9
38.9	6.8×10^9

Figure R5.3K shows the Arrhenius plot of these data, from which the parameters in 5.4.10 were obtained.

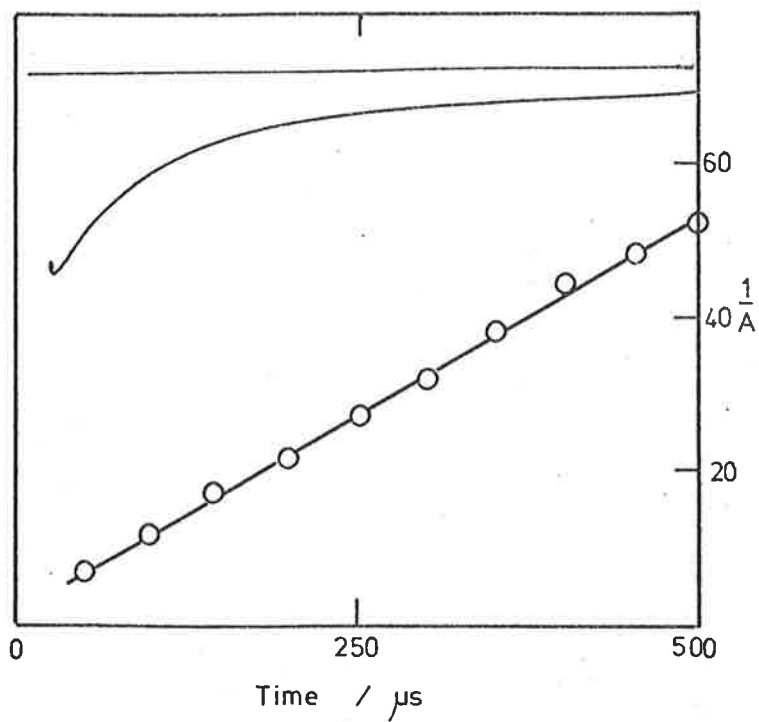


Fig. R5.4I

$$\lambda = 366 \text{ nm}$$

$$l = 5.0 \text{ cm}$$

$$2k = 5.5 \times 10^9$$

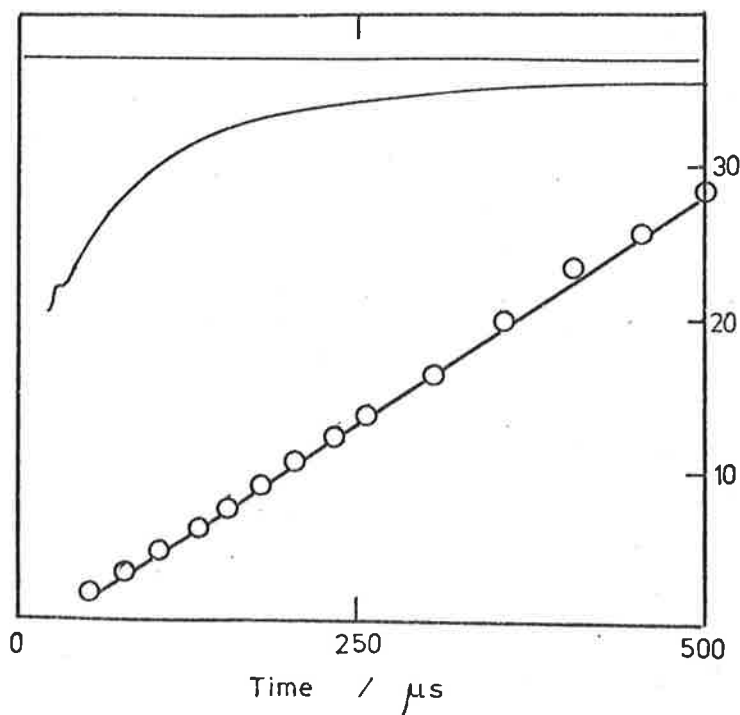


Fig. R5.4J

$$\lambda = 366 \text{ nm}$$

$$l = 10 \text{ cm}$$

$$2k = 5.8 \times 10^9$$

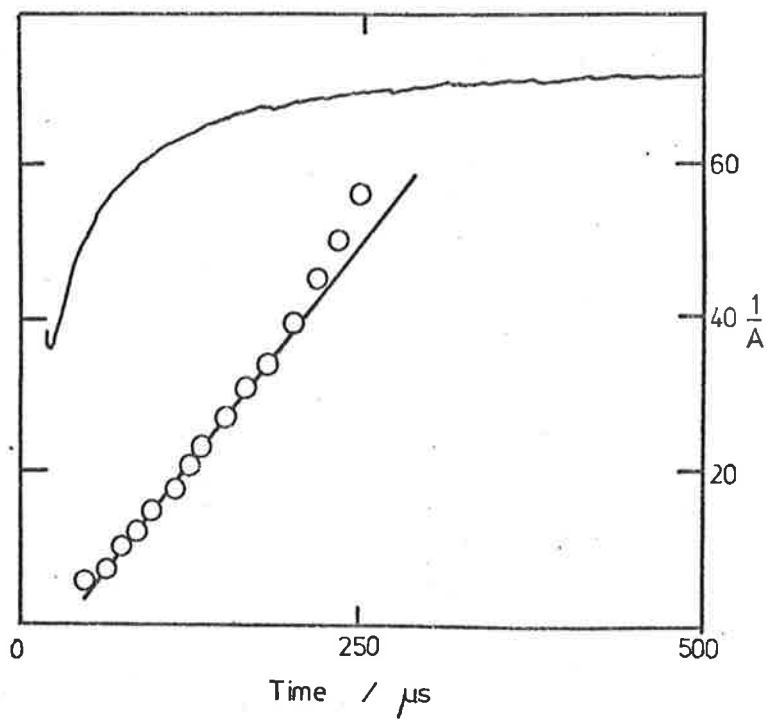


Fig. R5.4K

$\lambda = 366 \text{ nm}$
 $l = 5.0 \text{ cm}$
 $2k = 5.5 \times 10^9$

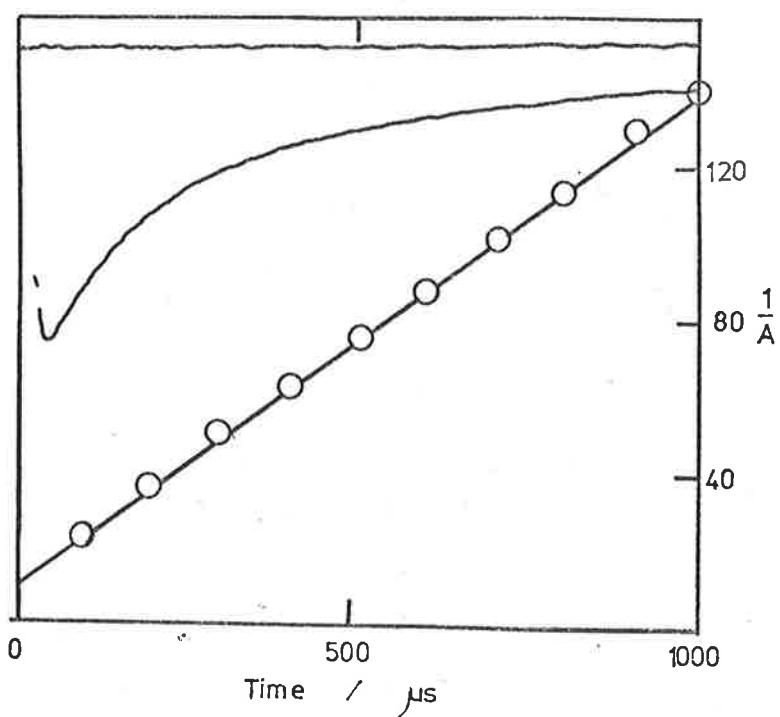


Fig. R5.5A

$\lambda = 405 \text{ nm}$
 $l = 10 \text{ cm}$
 $2k = 8.7 \times 10^9$

R5.5 DECAY OF I_2^-

R5.5.1 Deaerated iodide solution

Fig. R5.5A shows a typical oscilloscope trace and second order plot resulting from flash photolysis of deaerated iodine/iodide solution as observed at 405 nm. The decay of I_2^- is good second order with a rate constant of $(9.2 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ calculated using $\epsilon = \epsilon_{I_2^-} - \frac{1}{2} \epsilon_{I_3^-} = 9300$.

Fig. R5.5B shows the same solution at 313 nm where I_3^- formation is observed. Second order kinetics are again obeyed with a rate constant of $(8.0 \pm 2) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ using $\epsilon = \frac{1}{2} \epsilon_{I_3^-} - \epsilon_{I_2^-} = 7300$.

R5.5.2 Aerated iodine/iodide solution

In aerated solution the decay of I_2^- is described by



Fig. R5.5C shows an oscilloscope trace (at 405 nm), $1/\text{absorbance}$ against time points and a solid line which is a best fit to the experimental points calculated assuming $2k_1 = 8.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_2 = 4 \times 10^3 \text{ s}^{-1}$. The small permanent change in absorbance shows that reaction (1) is not the only one of importance.

R5.5.3 Deaerated iodide solution

The decay of I_2^- in deaerated iodide solution is illustrated in Fig. R5.5D. The best fit curve through the experimental points is simulated using the following scheme



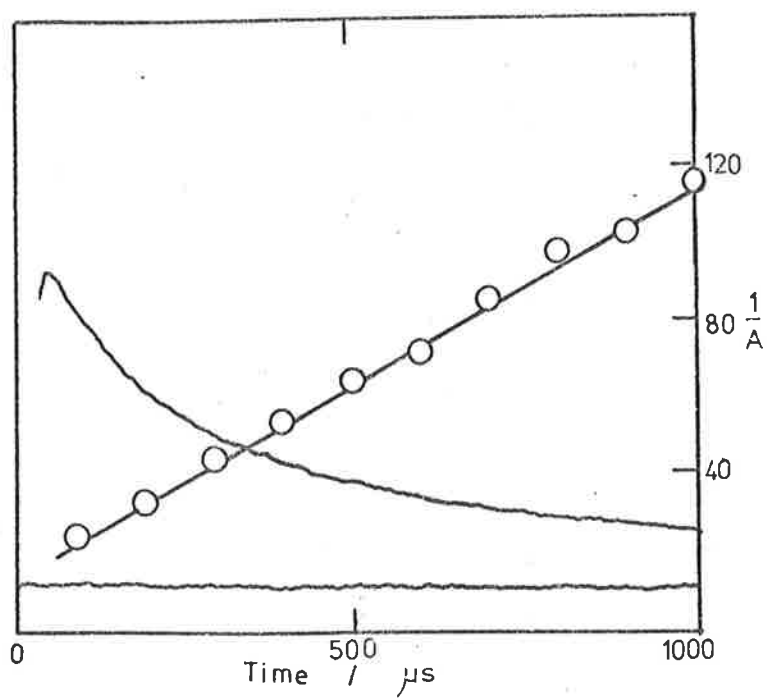


Fig. R5.5B

$\lambda = .313 \text{ nm}$

$l = 10 \text{ cm}$

$2k = 7.7 \times 10^9$

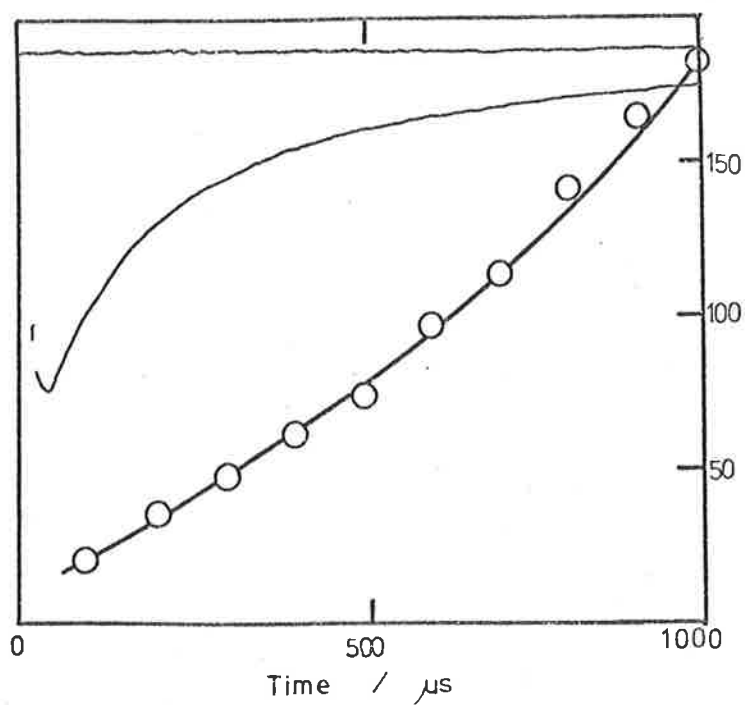


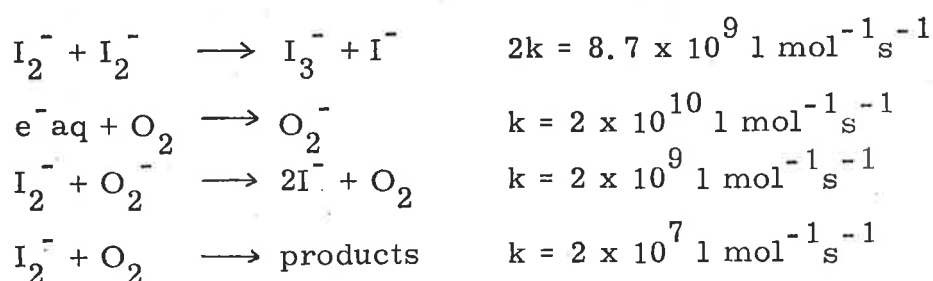
Fig. R5.5C

$\lambda = 405 \text{ nm}$

$l = 10 \text{ cm}$

R5.5.4 Aerated iodide solution

Fig. R5.5E shows a typical oscilloscope trace produced by flash photolysis of aerated iodide solution, and corresponding $1/\text{absorbance}$ against time points. The curve is calculated using rate constants in the scheme below

R5.5.5 Acidified deaerated iodide solution

The decay of I_2^- at 405 nm is good second order. Fig. R5.5F shows a typical oscilloscope trace and second order plot.

R5.5.6 Temperature dependence of I_2^- disproportionation rate constant

The effect of temperature on the rate of the second order decay of I_2^- from deaerated iodine solutions (see R5.5.1) was studied from 15 to 40°C. Table R5.5A lists the second order rate constant as a function of temperature.

Table R5.5A

Temp °C	$2k (\text{I}_2^- + \text{I}_2^-)$ ($\text{l mol}^{-1} \text{s}^{-1}$)
14.9	7.6×10^9
24.4	9.1×10^9
30.6	10.1×10^9
40.2	12.0×10^9

Fig. R5.3K is an Arrhenius plot of $\log_{10} 2k$ against the reciprocal of absolute temperature. The parameters listed in 5.5.6 were obtained.

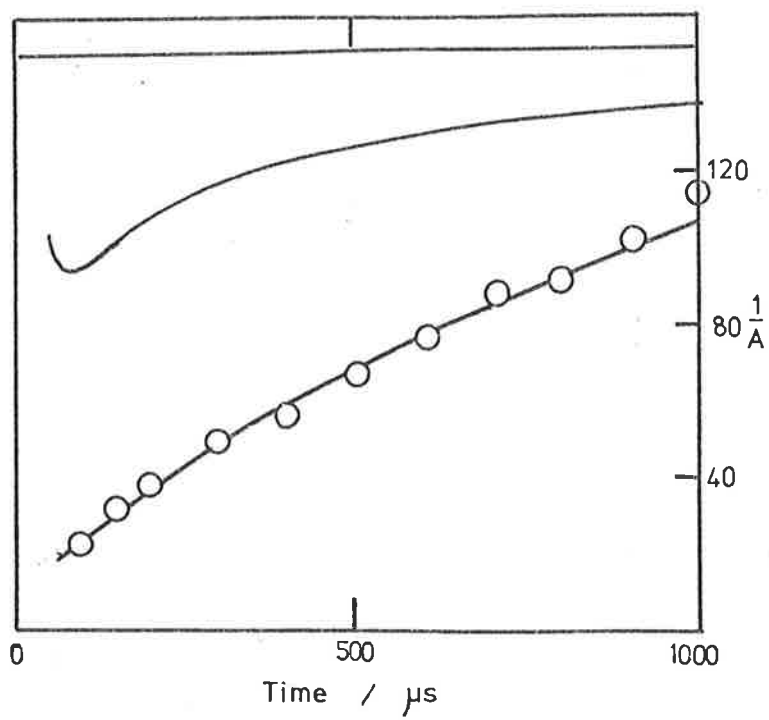


Fig. R5.5D

$\lambda = 405 \text{ nm}$

$l = 10 \text{ cm}$

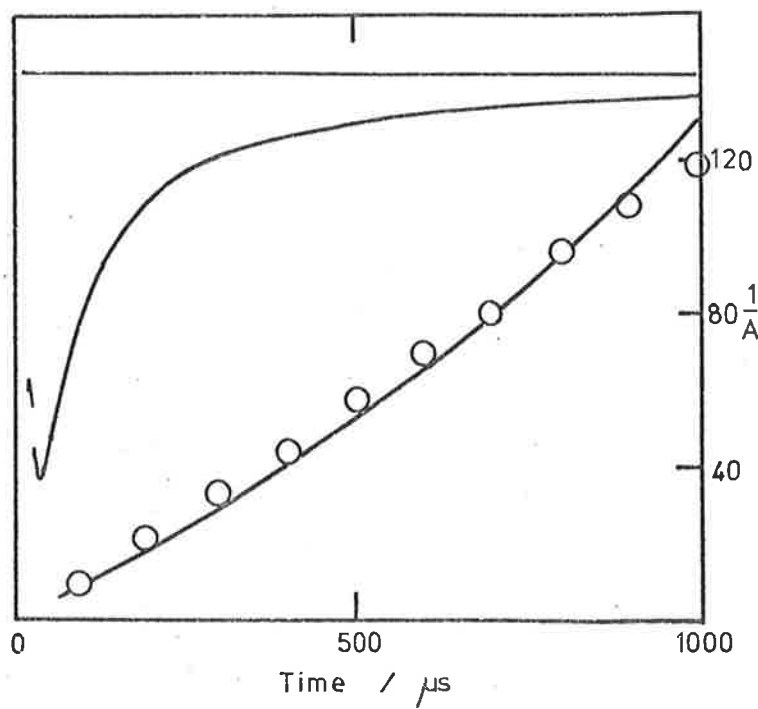
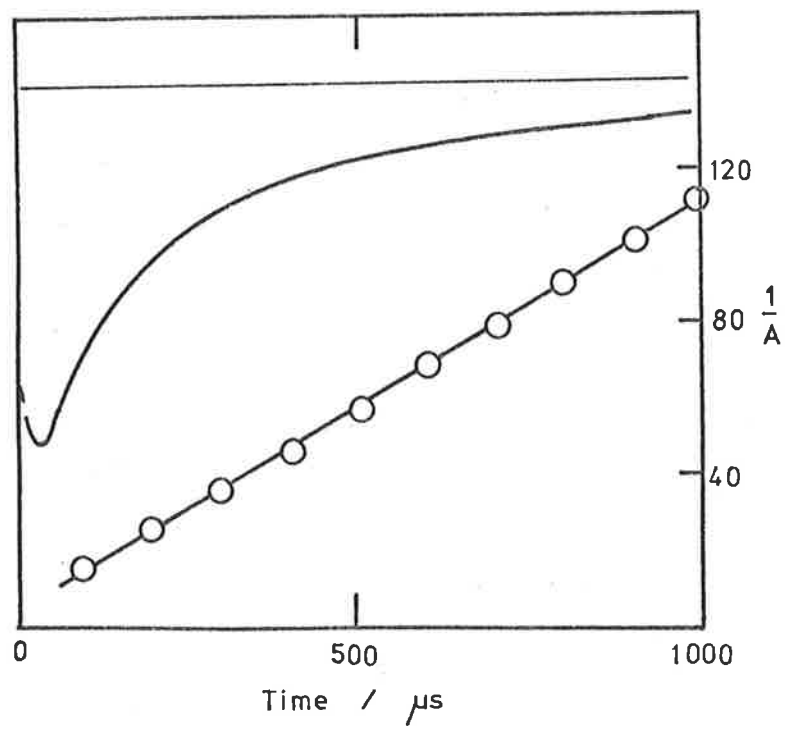


Fig. R5.5E

$\lambda = 405 \text{ nm}$

$l = 10 \text{ cm}$



Fig, R5.5F

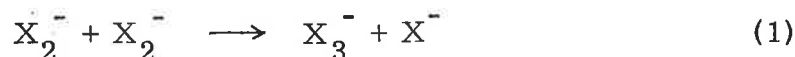
$$\lambda = 405 \text{ nm}$$

$$l = 10 \text{ cm}$$

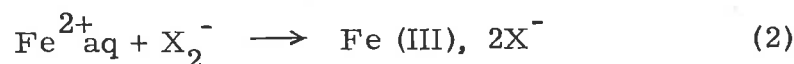
$$2k = 8.0 \times 10^9$$

SECTION R13 SUPPLEMENTARY RESULTSREDOX REACTIONSR13.1 IRON (II)R13.1.1 Rate and temperature dependence $\text{Fe}^{2+} + \text{X}_2^-$

A solution containing Cl^- or Br^- ($10^{-1} \text{ mol l}^{-1}$), H^+ ($10^{-1} \text{ mol l}^{-1}$) and $\text{Fe}^{3+}_{\text{aq}}$ ($10^{-4} = 5 \times 10^{-4} \text{ mol l}^{-1}$) produces Cl_2^- or Br_2^- (Section 2.3.3). In the absence of added $\text{Fe}^{2+}_{\text{aq}}$, Cl_2^- and Br_2^- decay by disproportionation (1) (See Sections 5.3.9, 5.4.9).



In the presence of $\text{Fe}^{2+}_{\text{aq}}$ ($5 \times 10^{-4} - 10^{-2} \text{ mol l}^{-1}$) decay is more rapid.



Figures R13.1A and R13.1B show typical oscilloscope traces (volts vs time) and corresponding optical densities. The solid line through the experimental optical densities is calculated assuming concurrent second order disproportionation and pseudo first order reactions, and is a better fit to the experimental data than either a pure first or second order decay (dotted lines).

The absorbance against time curves for the ferrous systems are complicated by the presence or formation of $\text{FeBr}^{2+}_{\text{aq}}$ and $\text{FeCl}^{2+}_{\text{aq}}$ which absorb in the same region ($\lambda = 300 - 400 \text{ nm}$) as Br_2^- and Cl_2^- . In situations where a 1:1 stoichiometry does not exist for X_2^- formed; FeX^{2+} removed or X_2^- removed; FeX^{2+} reformed (e.g. 13.1.3) the analysis is complex and is best treated by a simulation of the optical density against time curve using known parameters of the system (Appendix 4.4). Figures R13.1C and R13.1D show this computed curve in comparison with the curve calculated for a simple first plus second order decay. In each case the fit of the rigorously derived absorbance against time curve is

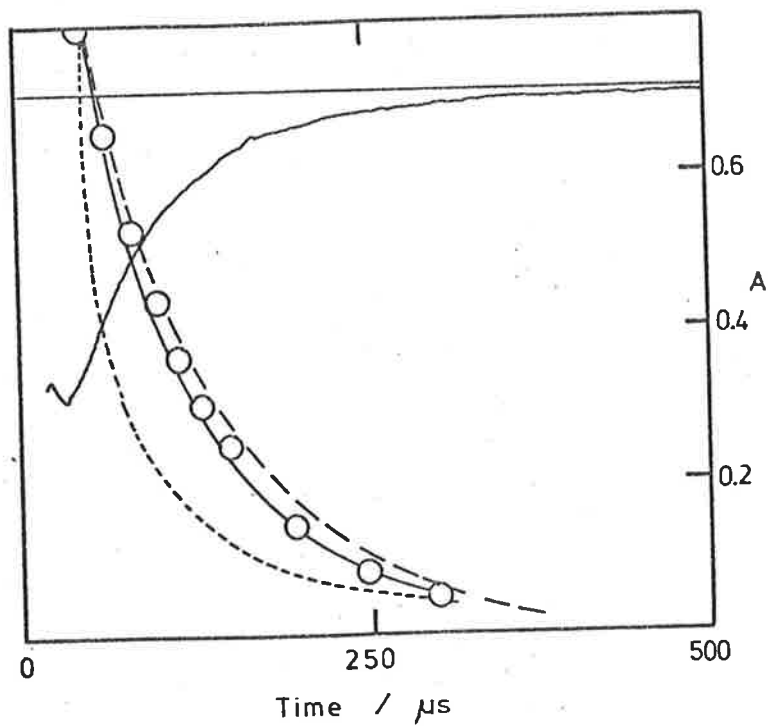
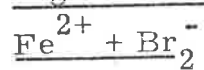


Fig. R13.1A



365 nm

- 2nd order
- 1st order
- 1st + 2nd
- Expt.

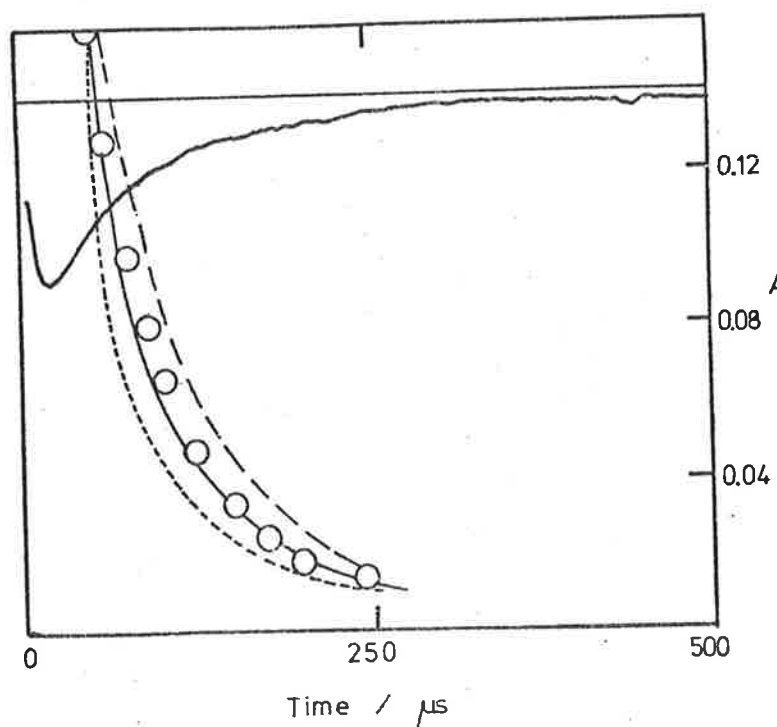
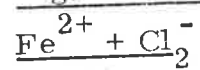


Fig. R13.1B



365 nm

- 2nd order
- 1st order
- 1st + 2nd
- Expt.

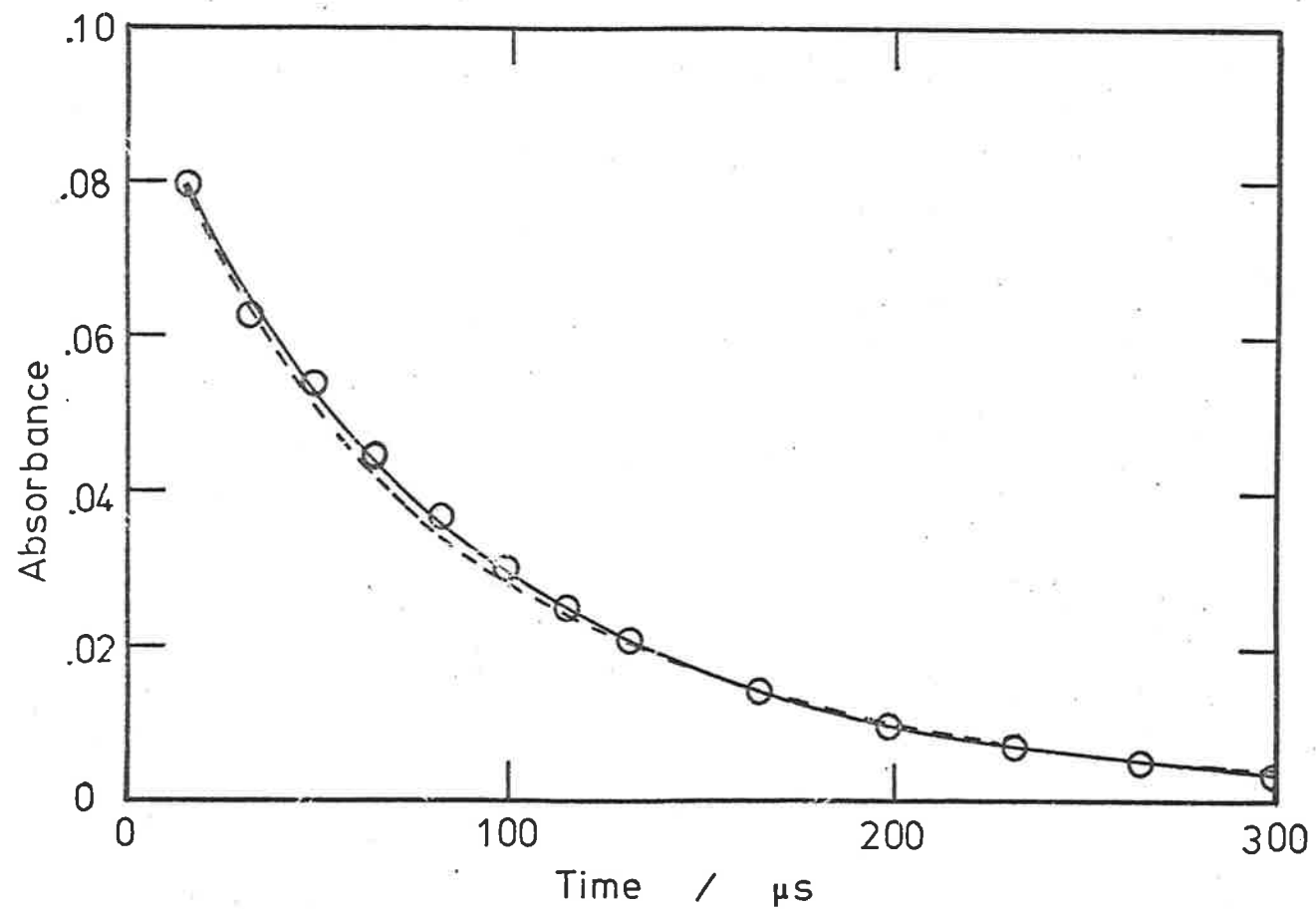


Fig. R13.1C $\text{Fe}^{2+}\text{aq} + \text{Br}_2^-$, Comparison of Fits (From Fig. R13.1A)
 Experimental Absorbances (O), Rigorously Derived Fit (————)
 Fit of First + Second Order (-----).

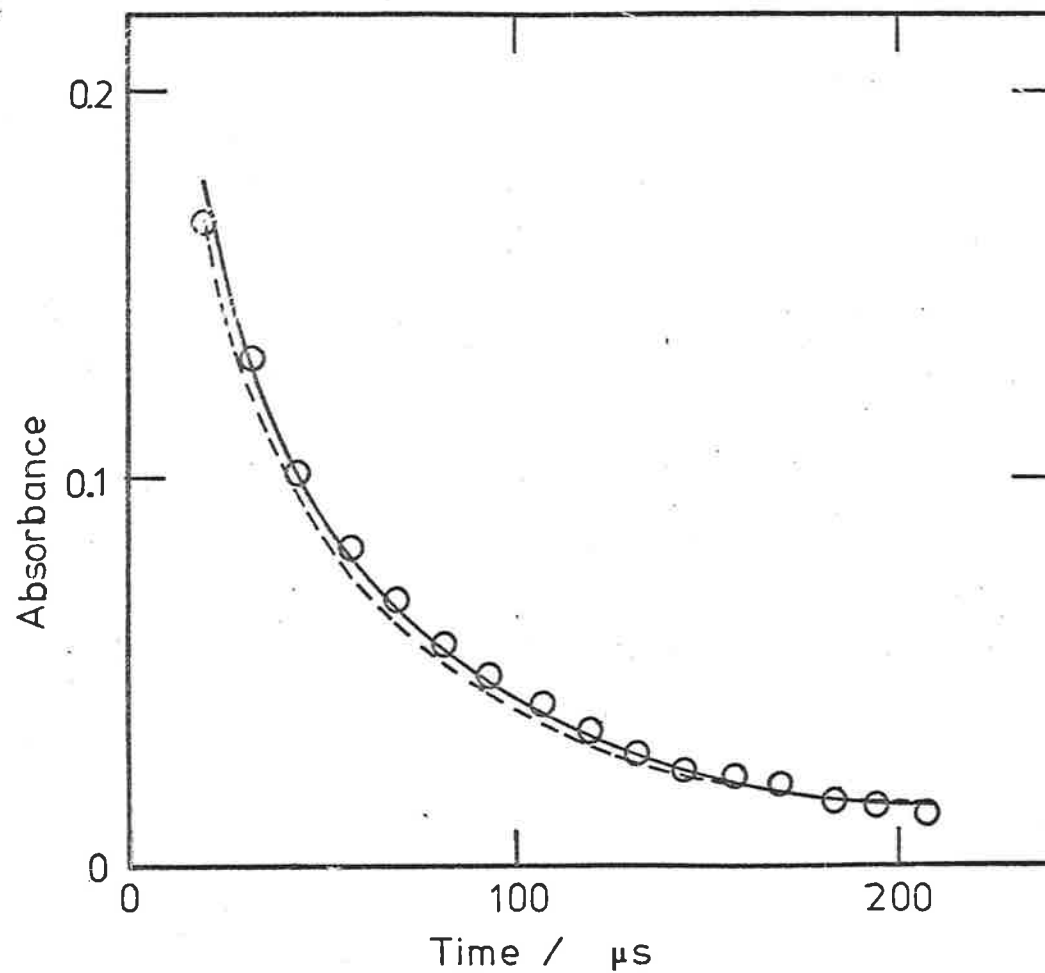


Fig. R13.1D $\text{Fe}^{2+}_{\text{aq}} + \text{Cl}_2^-$, Comparison of Fits (From Fig. R13.1B)

Experimental Absorbances (O), Rigorously Derived Fit (—)

Fit of First + Second Order (---).

R17.

slightly better than the fit of the curve neglecting contributions from FeX^{2+} but the values of the first order rate constants necessary to fit the curves are little different. (See Table R13.1A)

Table R13.1A
Fit of OD against time data

Best 1st order $k_{\text{Br}_2^-}^a$	$1.03 \times 10^4 \text{ s}^{-1}$
Best 1st order $k_{\text{Br}_2^-}^b$	$1.00 \times 10^4 \text{ s}^{-1}$
Best 1st order $k_{\text{Cl}_2^-}^a$	$8.3 \times 10^3 \text{ s}^{-1}$
Best 1st order $k_{\text{Cl}_2^-}^b$	$8.0 \times 10^3 \text{ s}^{-1}$

Notes:

(a) rigorously derived to fit data in Fig. R13.1A

(b) derived by ignoring interference from FeX^{2+}

Differences between the two estimates were not considered significant and all rate data were derived by ignoring the complication of FeX^{2+} absorbance. Fig. R13.1E shows the dependence of the pseudo first order rate constant for reaction of Br_2^- with $\text{Fe}^{2+}_{\text{aq}}$ on the concentration of $\text{Fe}^{2+}_{\text{aq}}$ at a variety of temperatures. Fig. R13.1F shows the corresponding plots for $\text{Fe}^{2+}_{\text{aq}} + \text{Cl}_2^-$. In each case the plots are linear over the entire range of $[\text{Fe}^{2+}_{\text{aq}}]$; the derived bimolecular rate constants are listed in Table R13.1B.

Table R13.1B
 $\text{Fe}^{2+}_{\text{aq}} + \text{X}_2^-$: Bimolecular rate constants

Temperature $^{\circ}\text{C}$	$k_2 (\text{Fe}^{2+}_{\text{aq}} + \text{Br}_2^-)$ $1 \text{ mol}^{-1} \text{ s}^{-1}$	$k_2 (\text{Fe}^{2+}_{\text{aq}} + \text{Cl}_2^-)$ $1 \text{ mol}^{-1} \text{ s}^{-1}$
15	$(2.7 \pm 0.3) \times 10^6$	$(9.6 \pm 1) \times 10^6$
25	$(3.7 \pm 0.4) \times 10^6$	$(1.4 \pm 0.14) \times 10^7$
31	$(4.5 \pm 0.5) \times 10^6$	$(1.7 \pm 0.2) \times 10^7$
40	$(5.9 \pm 0.6) \times 10^6$	$(2.35 \pm 0.2) \times 10^7$

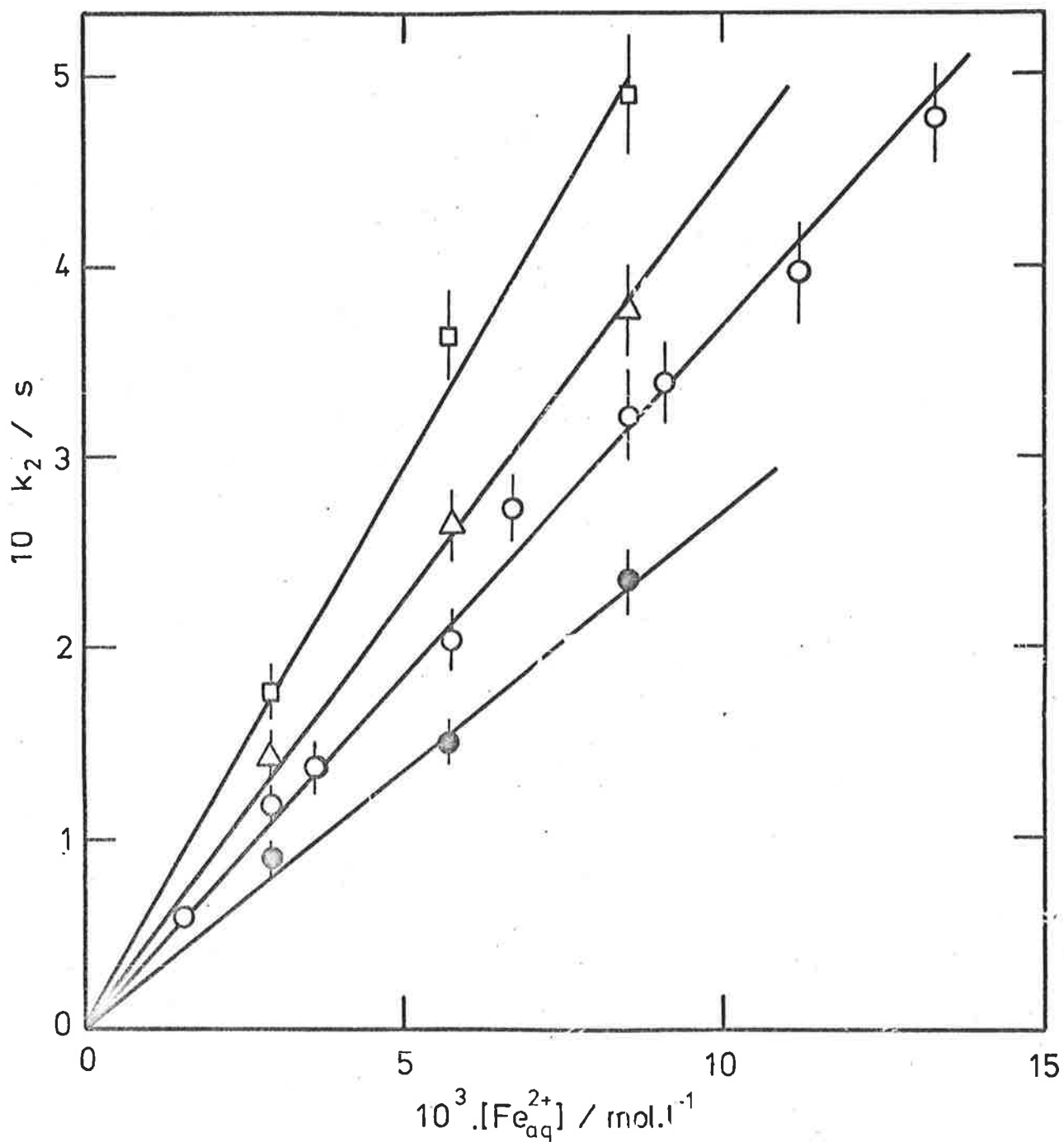


Fig. R13.1E $\text{Fe}_{\text{aq}}^{2+} + \text{Br}_2^-$, Dependence of Pseudo First Order Rate Constant on $[\text{Fe}_{\text{aq}}^{2+}]$.

($\bullet$, 15°C ; $\circ$, 25°C ; $\triangle$, 31°C ; $\square$, 40°C)

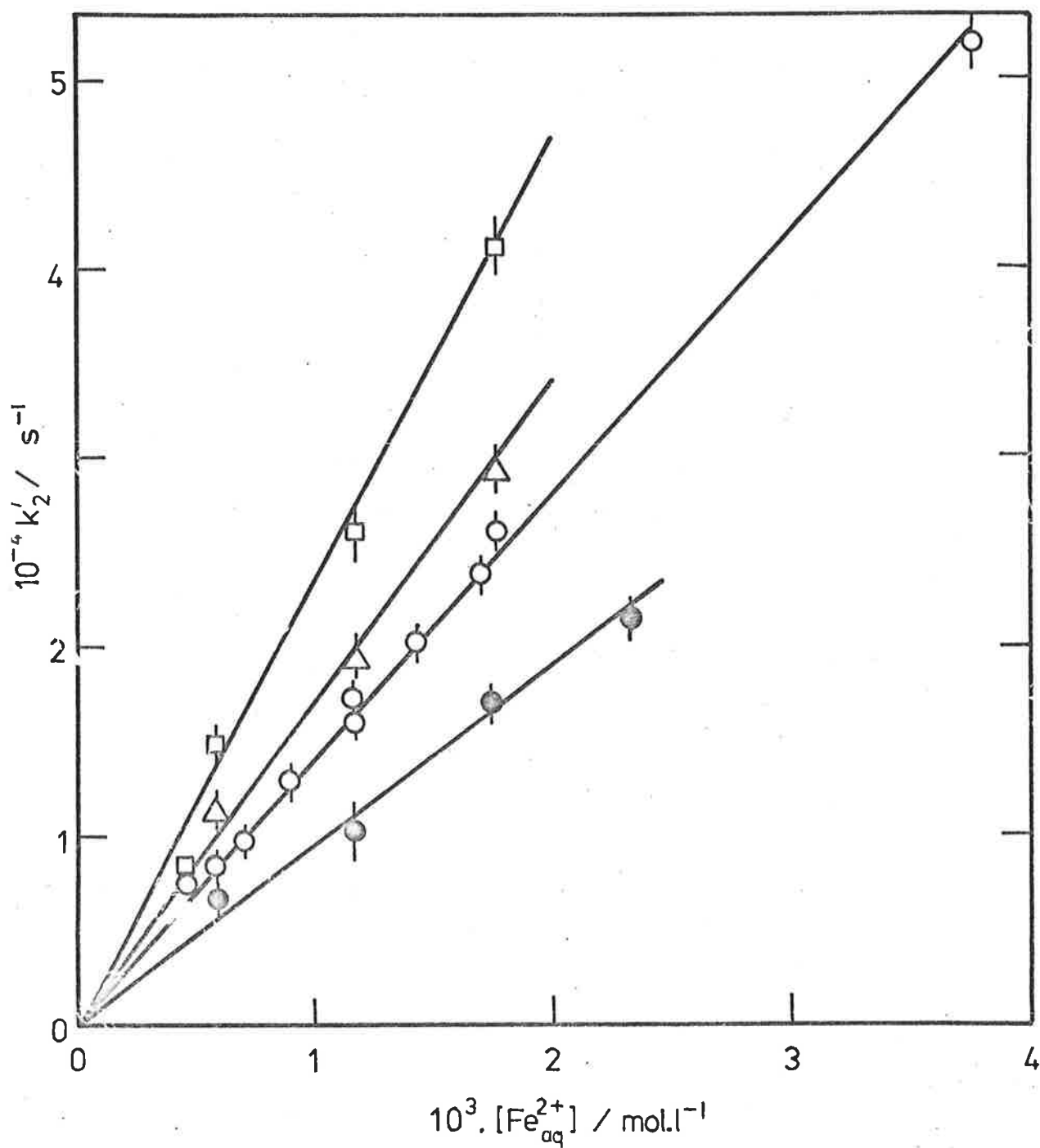


Fig. R13.1F $\text{Fe}^{2+}_{\text{aq}} + \text{Cl}_2$, Dependence of Pseudo First Order Rate Constant on $[\text{Fe}^{2+}_{\text{aq}}]$.
 (●, 15°C ; ○, 25°C ; △, 31°C ; □, 40°C)

R18.

Figure R13. 1G shows Arrhenius plots of $\log_{10}(k_2)$ against K^{-1} for Cl_2^- and Br_2^- . Within the limits of experimental error a linear relationship is observed. The derived activation parameters are listed in Table 13. 1A.

R13. 1. 2 Mechanism $\text{Fe}^{2+}_{\text{aq}} + \text{Br}_2^-$

The transient absorbance observed in the reaction of $\text{Fe}^{2+}_{\text{aq}}$ with Br_2^- exhibits the absorption spectrum shown in Fig. 13. 1A. A typical oscilloscope trace illustrating the decay of this transient produced from Br^- ($10^{-1} \text{ mol l}^{-1}$), H^+ ($10^{-1} \text{ mol l}^{-1}$) and $\text{Fe}^{2+}_{\text{aq}}$ ($10^{-2} \text{ mol l}^{-1}$), and the corresponding first order plot of $\log_{10}(\text{OD})$ against time are shown in Fig. R13. 1H. The pseudo first order rate constant for decay of this transient at 366 and 405 nm is $(9.0 \pm 0.2) \times 10^2 \text{ s}^{-1}$ in fair agreement with the value of $(7 \pm 2) \times 10^2 \text{ s}^{-1}$ extrapolated to 25°C from the values of Carlyle and Espenson (1969) for the ferrous catalyzed aquation of $\text{FeBr}^{2+}_{\text{aq}}$.

$$k_{\text{aq}} = k_a + k_b [\text{Fe}^{2+}_{\text{aq}}] + k_c / [\text{H}^+]$$

R13. 1. 3 Mechanism $\text{Fe}^{2+}_{\text{aq}} + \text{Cl}_2^-$

The transient observed on disappearance of Cl_2^- from a solution containing Cl^- ($10^{-1} \text{ mol l}^{-1}$), H^+ ($10^{-1} \text{ mol l}^{-1}$) and $\text{Fe}^{2+}_{\text{aq}}$ ($10^{-2} \text{ mol l}^{-1}$) exhibits the absorption spectrum shown in Fig. 13. 1C. A typical oscilloscope trace illustrating the decay of this transient and the corresponding first order plot of $\log_{10}(\text{OD})$ against time are shown in Fig. R13. 1I. The observed first order rate constant of $40 \pm 6 \text{ s}^{-1}$ is in good agreement with the value of 37 s^{-1} from the results of Moorhead and Sutin (1967) for the $\text{Fe}^{2+}_{\text{aq}}$ catalyzed aquation of $\text{FeCl}^{2+}_{\text{aq}}$.

$$k_{\text{aq}} = k_a + k_b [\text{Fe}^{2+}_{\text{aq}}] + k_c [\text{H}^+]$$

Similar plots for the reformation of $\text{FeCl}^{2+}_{\text{aq}}$ in a system where $\text{FeCl}^{2+}_{\text{aq}}$ is photolysed in the presence of $\text{Fe}^{2+}_{\text{aq}}$ (See Fig. 13. 1D) are also shown in Fig. R13. 1I. The derived rate constant of $41 \pm 4 \text{ s}^{-1}$

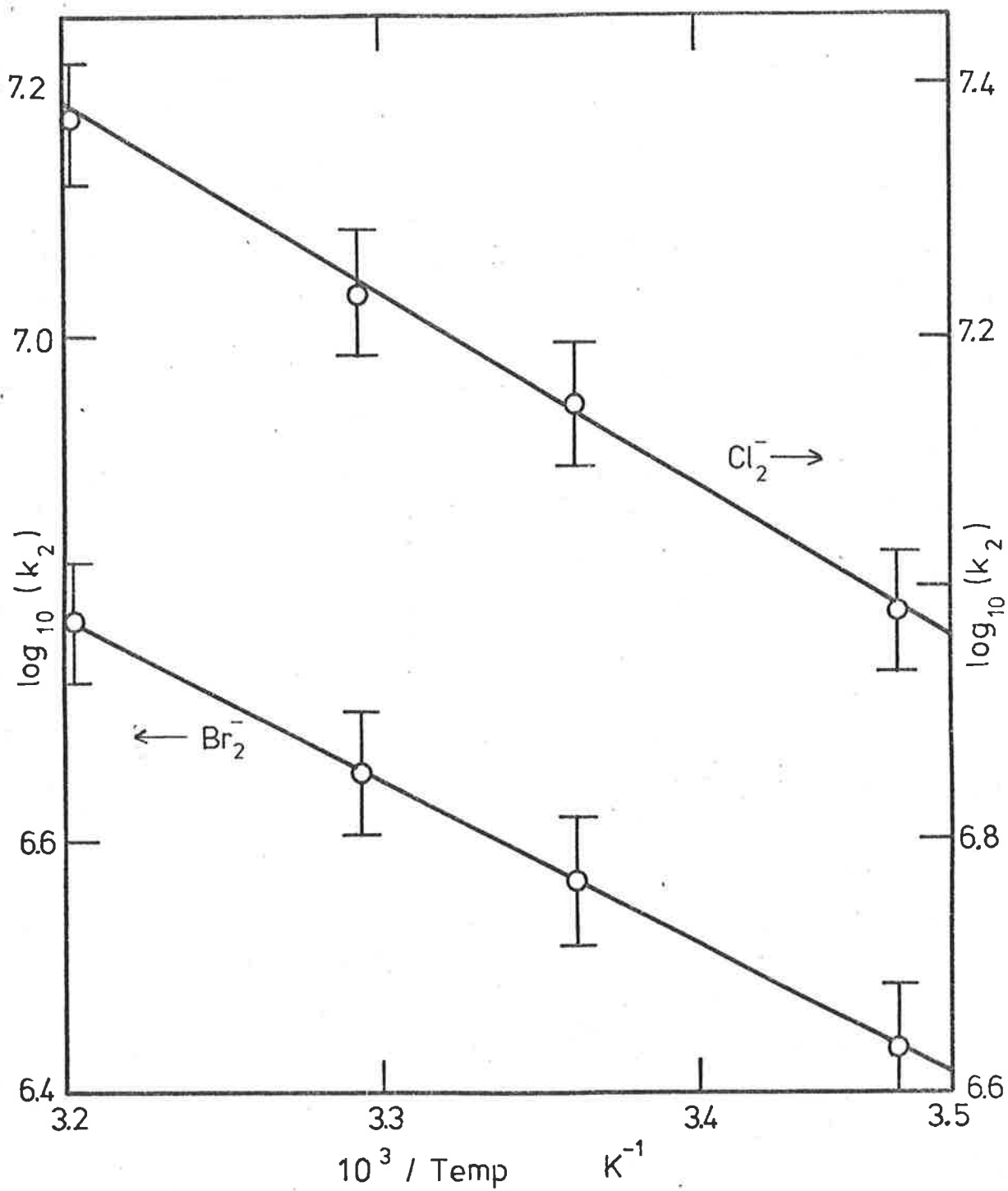
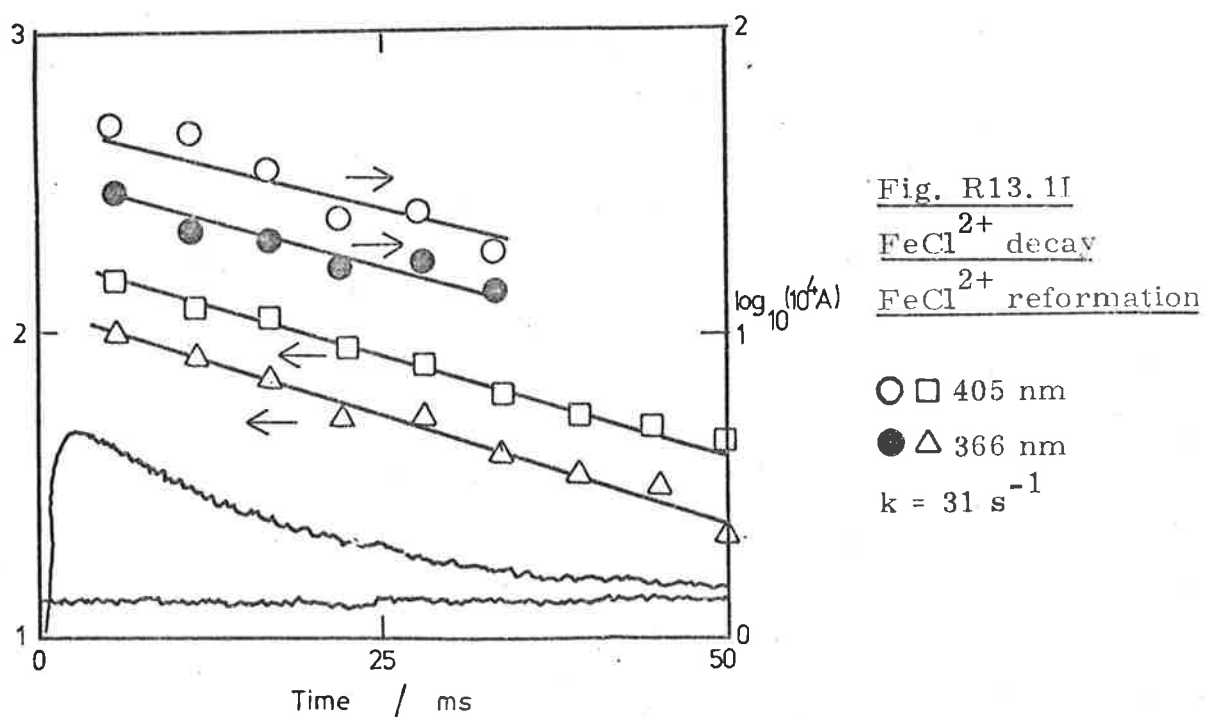
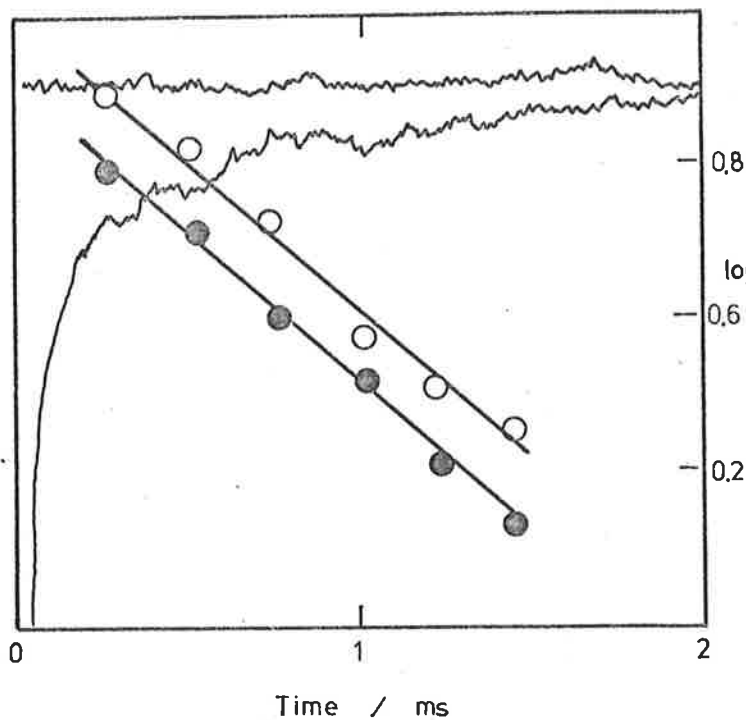


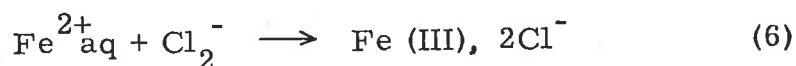
Fig. R13.1G Arrhenius Plots, $\text{Fe}^{2+} + \text{Br}_2^-$; $\text{Fe}^{2+} + \text{Cl}_2^-$



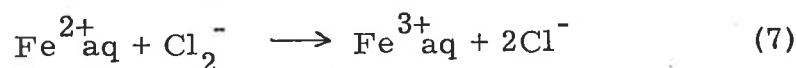
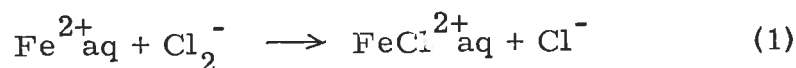
R19.

in good agreement with literature values and the rate of decay of $\text{FeCl}^{2+}_{\text{aq}}$.

The reaction of $\text{Fe}^{2+}_{\text{aq}}$ with Cl_2^- ,



proceeds by concurrent inner and outer sphere paths.



Observation of the absorbance after decay of Cl_2^- in a flash photolysed ferric chloride solution with and without $\text{Fe}^{2+}_{\text{aq}}$ allows the relative magnitudes of k_1 and k_7 to be calculated. (Sec 13.1.3). The experimental ratio k_1/k_7 and the absolute bimolecular rate constants k_6 , k_1 and k_7 are listed as a function of temperature in Table 13.1C. Fig. R13.1J shows Arrhenius plots of k_1 , k_7 and k_1/k_7 .

Table R13.1C

Temp °C	$k_6 = (k_1 + k_7)$ $\times 10^{-6}$	k_1/k_7	k_1 $\times 10^{-6}$ ($1 \text{ mol}^{-1} \text{ s}^{-1}$)	k_7 $\times 10^{-6}$ ($1 \text{ mol}^{-1} \text{ s}^{-1}$)
14	(9.6 ± 1)	$(0.37 \pm .05)$	(2.6 ± 0.5)	(7.0 ± 1.8)
25	(14 ± 1.5)	$(0.40 \pm .05)$	(4.0 ± 0.8)	(10.0 ± 3)
31	(17 ± 2)	$(0.45 \pm .05)$	(5.3 ± 1.2)	(11.7 ± 3.5)
40	(23.5 ± 2)	$(0.57 \pm .05)$	(8.5 ± 2)	(15.0 ± 4)

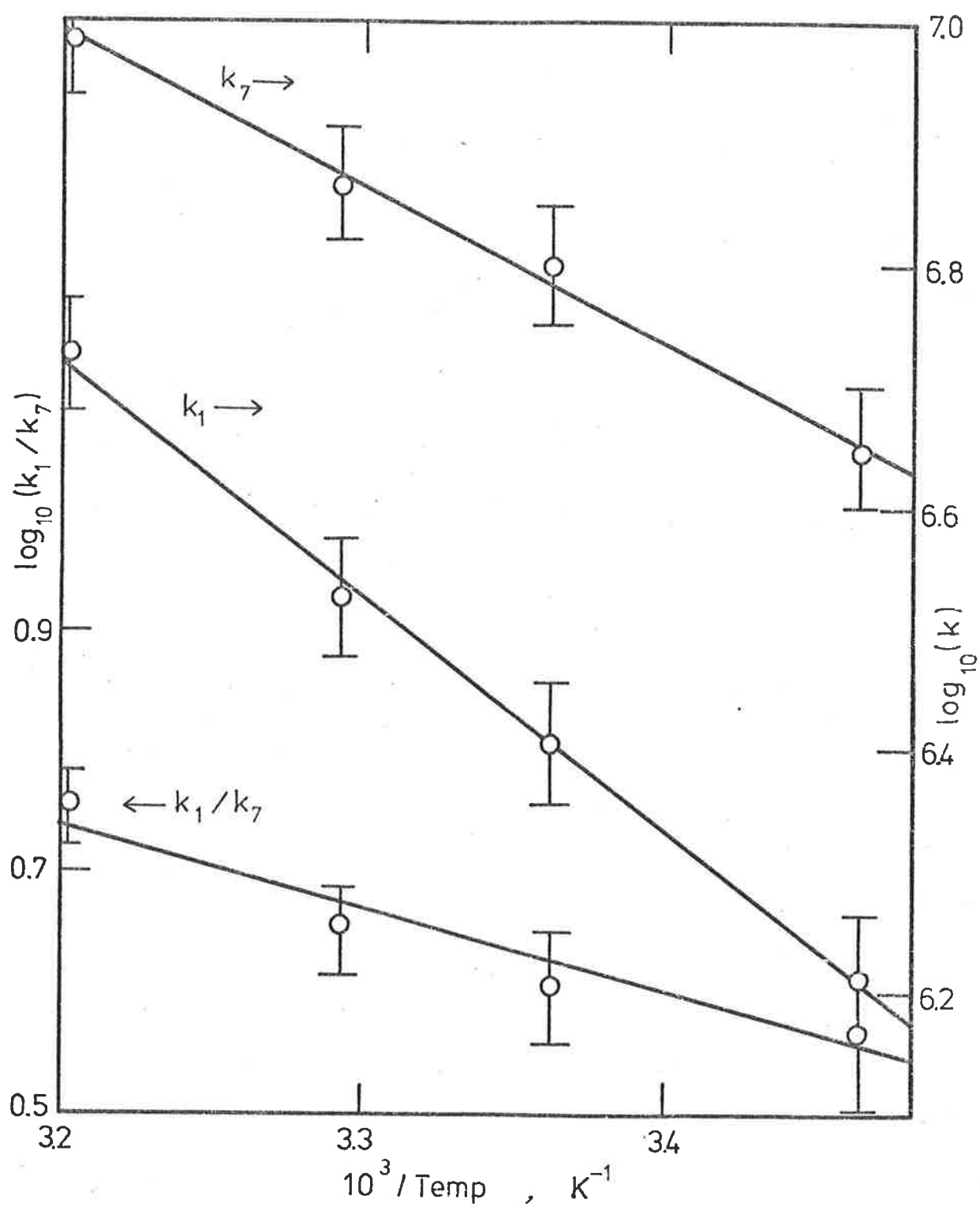


Fig. R13.1J Arrhenius Plots, $\text{Fe}^{2+} + \text{Cl}_2^-$:- k_1 , k_7 , k_1/k_7 .

R13.2 COBALT (II)R13.2.1 Br_2^- , I_2^-

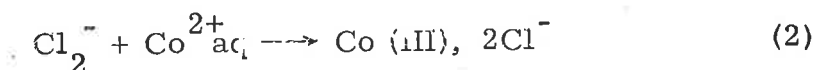
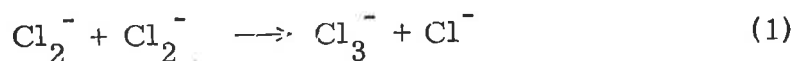
Addition of $5 \times 10^{-2} \text{ mol l}^{-1}$ of $\text{Co}^{2+}_{\text{aq}}$ to a deaerated solution of I^- ($2 \times 10^{-2} \text{ mol l}^{-1}$) and I_3^- ($\sim 5 \times 10^{-6} \text{ mol l}^{-1}$) reduces the amount of I_2^- formed but does not increase its decay rate. Fig. R13.2A shows a typical oscilloscope trace and the corresponding second order plot of OD^{-1} against time. The decay of I_2^- is good second order with a rate constant of $7.1 \pm 0.4 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in good agreement with that obtained in the absence of $\text{Co}^{2+}_{\text{aq}}$ (See 5.5). The upper limit for the rate of a reaction between $\text{Co}^{2+}_{\text{aq}}$ and I_2^- is $5 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

Similarly $\text{Co}^{2+}_{\text{aq}}$ ($5 \times 10^{-2} \text{ mol l}^{-1}$) produces no increase in the rate of decay of Br_2^- from a Br^- ($10^{-1} \text{ mol l}^{-1}$), H^+ ($10^{-1} \text{ mol l}^{-1}$) and Br_3^- ($\sim 10^{-4} \text{ mol l}^{-1}$) solution. Fig. R13.2B shows an oscilloscope trace and the corresponding second order plot. The decay of Br_2^- is good second order with a rate constant of $(5.4 \pm 0.6) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in good agreement with the rate constant of the Br_2^- disproportionation reaction (see Table 5.3A). The rate constant of a reaction between $\text{Co}^{2+}_{\text{aq}}$ and Br_2^- must be less than $2 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

R13.2.2 Rate and temperature dependence $\text{Co}^{2+}_{\text{aq}} + \text{Cl}_2^-$

Flash photolysis of a chlorine solution in $0.1 \text{ mol l}^{-1} \text{ Cl}^-$ and $0.1 \text{ mol l}^{-1} \text{ H}^+$ produces about $10^{-5} \text{ mol l}^{-1}$ concentrations of Cl_2^- decaying by a good second order reaction with a rate constant of $5.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ (See 5.4.7).

Addition of $\text{Co}^{2+}_{\text{aq}}$ ($10^{-2} - 5 \times 10^{-2} \text{ mol l}^{-1}$) increases the rate of decay of Cl_2^- which can then be analyzed in terms of competing first and second order processes.



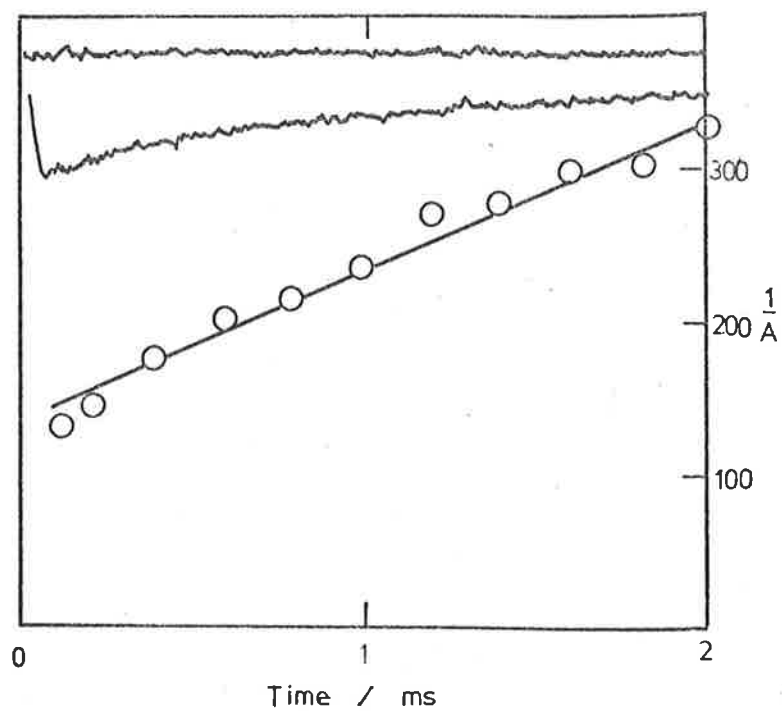
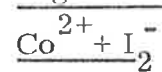


Fig. R13.2A



365 nm

$$2k = 7.5 \times 10^9$$

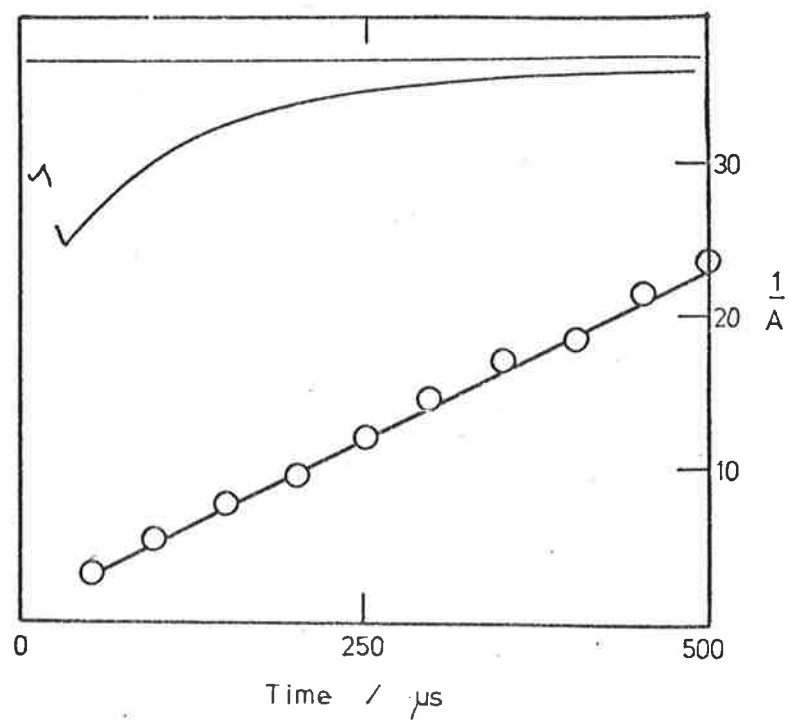
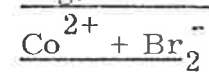


Fig. R13.2B



365 nm

$$2k = 5.2 \times 10^9$$

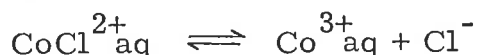
R21.

Fig. R13.2C shows a typical oscilloscope trace and corresponding absorbance against time points. The solid line is calculated assuming concurrent first and second order reactions and is a better fit than either simple first or second order kinetics (dotted lines).

Fig. R13.2D shows a plot of k_2' the pseudo first order rate constant against $[\text{Co}^{2+}_{\text{aq}}]$ at 25°C . The second order rate constant, k_2 , is independent of $[\text{Co}^{2+}_{\text{aq}}]$ between 1 and $5 \times 10^{-2} \text{ mol l}^{-1}$. If it is assumed that the pseudo first order rate constant is proportional to $[\text{Co}^{2+}_{\text{aq}}]$ at other temperatures, then a plot of $\log_{10} k_2'$ at fixed $[\text{Co}^{2+}_{\text{aq}}]$ against $1/K$ gives the same slope as a plot of $\log_{10} k_2$ against $1/K$. Fig. R13.2E shows an Arrhenius plot of $\log_{10} k_2$ at $[\text{Co}^{2+}_{\text{aq}}] = 2 \times 10^{-2} \text{ mol l}^{-1}$. The derived activation parameters are listed in 13.2.2

R13.2.3 Mechanism $\text{Co}^{2+}_{\text{aq}} + \text{Cl}_2^-$

Analysis of the decay of $\text{CoCl}^{2+}_{\text{aq}}$ observed at 297 nm or 313 nm shows two processes. The initial faster decay is first order with a rate constant of $59 \pm 2 \text{ s}^{-1}$ (See R13.2F).

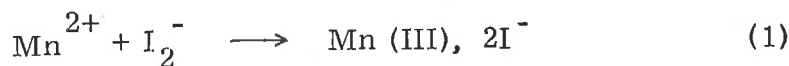


The slower process has a half life of $\sim 50 \text{ ms}$ and is attributed to a redox process (See 13.2.3).

R13.3 MANGANESE (II)

R13.3.1 I_2^-

Typical oscilloscope traces showing the decay of I_2^- in the presence of $5 \times 10^{-2} \text{ mol l}^{-1} \text{ Mn}^{2+}_{\text{aq}}$, and a second order plot of $1/\text{absorbance}$ against time are shown in Fig. R13.3A. The decay of I_2^- is good second order with a rate constant of $7.7 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in excellent agreement with the value obtained in the absence of $\text{Mn}^{2+}_{\text{aq}}$. An upper limit of $2 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ can be calculated for the rate constant or reaction (1).



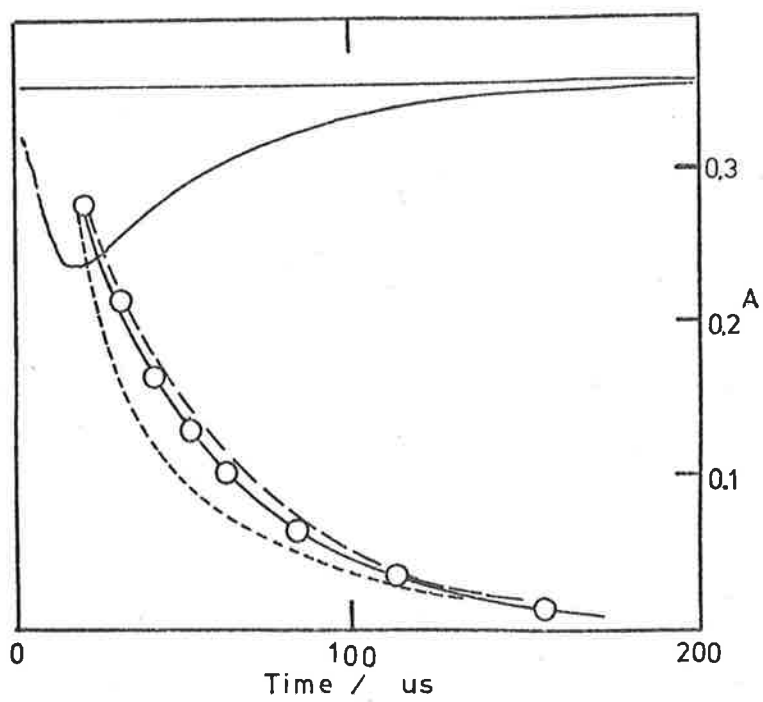
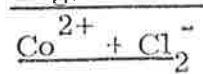


Fig. R13.2C



365 nm

.....2nd order

---1st order

—1st + 2nd

○ Expt.

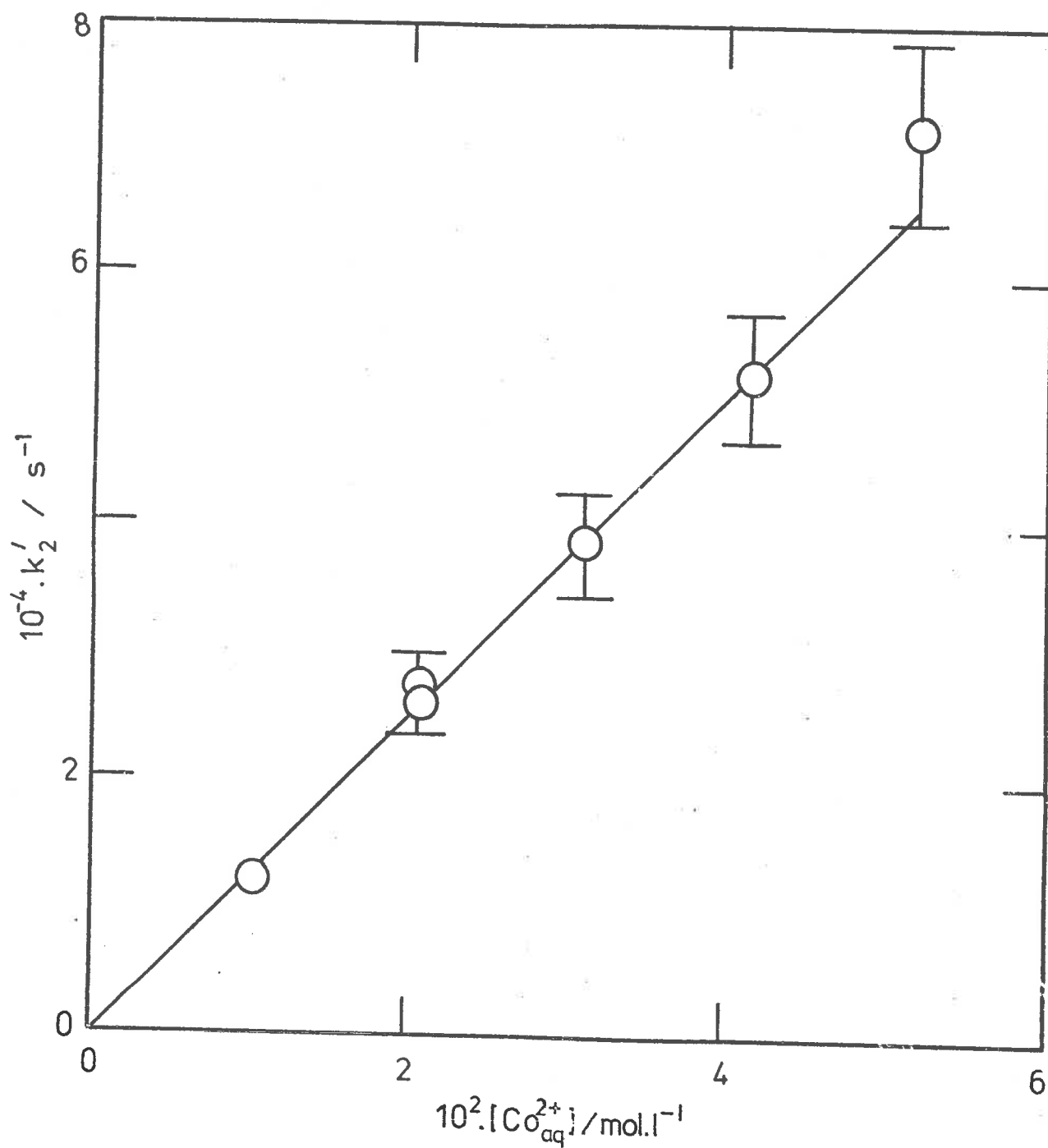


Fig. R13.2D $\text{Co}^{2+}_{\text{aq}} + \text{Cl}_2^-$, Dependence of Pseudo First Order Rate Constant on $[\text{Co}^{2+}_{\text{aq}}]$, at 25°C .

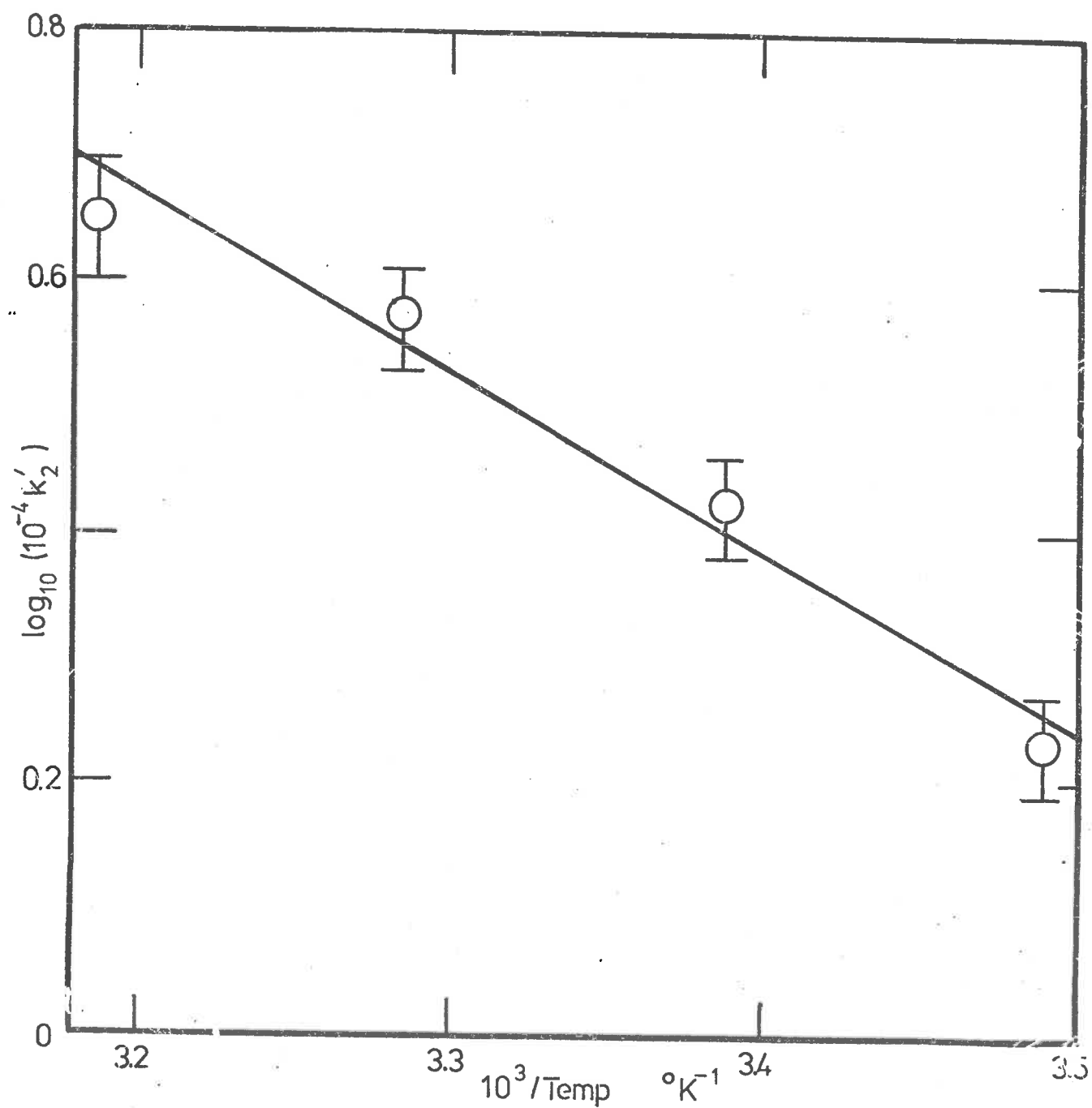


Fig. P-3.2E $\text{Co}^{2+}_{\text{aq}} + \text{Cl}_2^-$, Arrhenius Plot ($[\text{Co}^{2+}_{\text{aq}}] = 2 \times 10^{-2} \text{ mol l}^{-1}$)

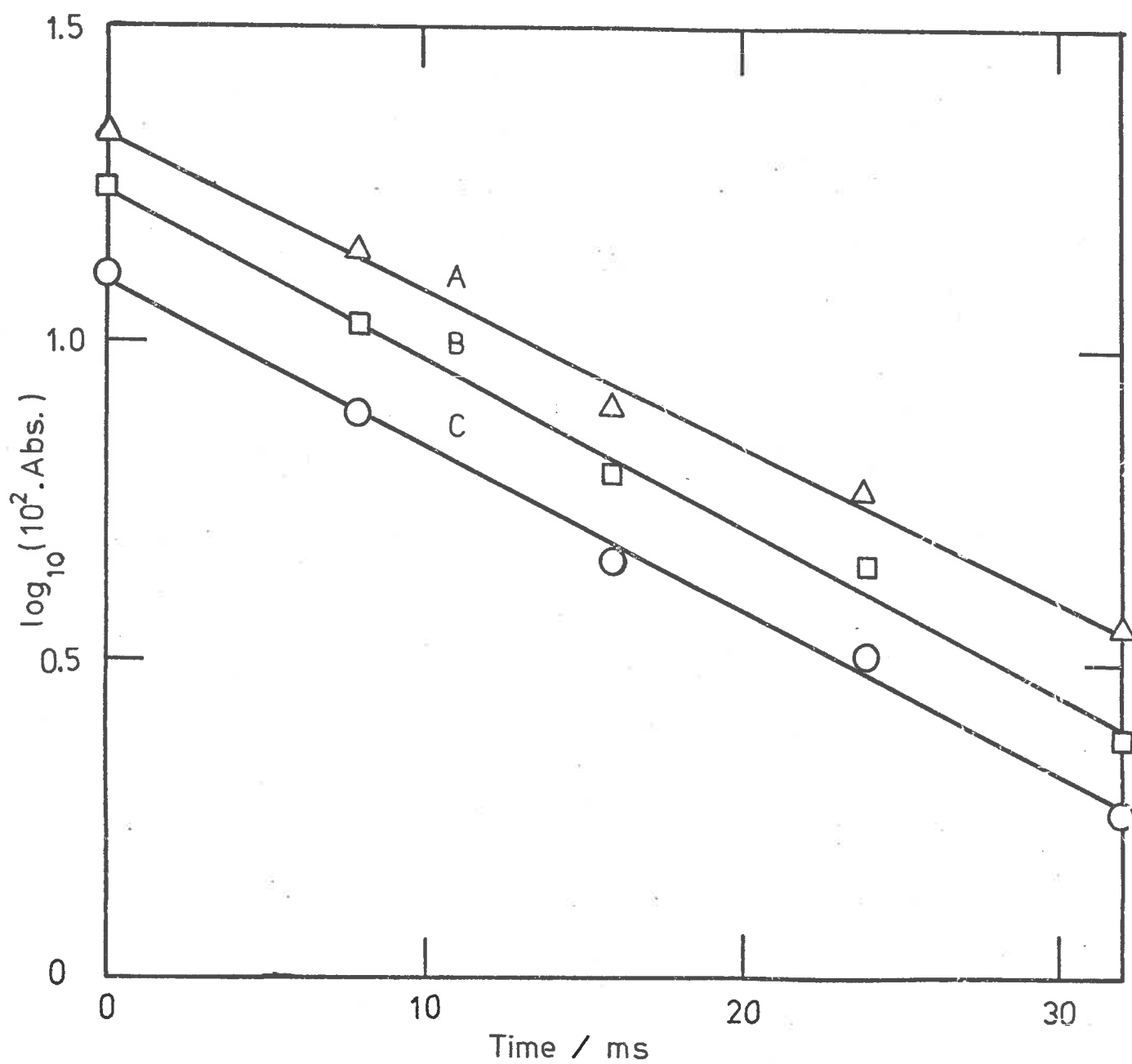


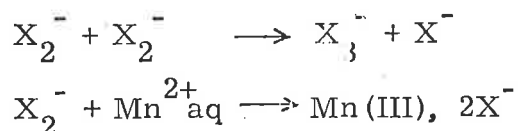
Fig. R13.2F $\text{Co}^{2+}_{\text{aq}} + \text{Cl}_2^-$, Initial Rapid Decay of Co(III) Transient
 (Δ , 297 nm ; $\square$, 313 nm ; $\bigcirc$, 366 nm)

R13.3.2 Rates and temperature dependence $\text{Mn}^{2+}_{\text{aq}} + \text{X}_2^-$

Oscilloscope traces and computed and observed plots of absorbance against time are shown in Figs. R13.3B and R13.3C for Br_2^- and Cl_2^- . The fit of the computed curve for competing first and second order reactions is better than the fit of simple first or second order kinetics. The magnitude of the first order component was determined with at least 5 different $\text{Mn}^{2+}_{\text{aq}}$ concentrations in the range 10^{-3} to $2 \times 10^{-2} \text{ mol l}^{-1}$ and at 4 temperatures between 15 and 40°C . The dependence of the pseudo first order component on $\text{Mn}^{2+}_{\text{aq}}$ is discussed in 13.3.3 and 13.3.4 and shown in Fig. 13.3A and 13.3B.

R13.3.3 $\text{Mn}^{2+}_{\text{aq}}$ dependence

To investigate the possibility that the fall in the apparent bimolecular rate constant for reaction (2), as $[\text{Mn}^{2+}_{\text{aq}}]$ increased, was due to ionic strength differences, the pseudo first order component k_2' was determined at $[\text{Mn}^{2+}_{\text{aq}}] = 2 \times 10^{-3} \text{ mol l}^{-1}$ with $I = 0.21 \text{ mol l}^{-1}$ and $I = 0.26 \text{ mol l}^{-1}$.



For Cl_2^- the experimentally observed rate constants were $(1.6 \pm 0.1) \times 10^4 \text{ s}^{-1}$ and $(1.5 \pm 0.1) \times 10^4 \text{ s}^{-1}$. No significant difference is observed.

R13.3.4 Activation parameters

Activation parameters for the overall reaction of $\text{Mn}^{2+}_{\text{aq}}$ with Br_2^- and Cl_2^- can be attained from a temperature dependence of the reciprocal of the slopes of the reciprocal plots (see Figs. 13.3C and 13.3D). Plots of $\log_{10}(K_{\text{obs.}}k)$ against $1/T$ $^\circ\text{K}$ are shown in Fig. R13.3D. The derived activation parameters are given in Table. 13.3A.

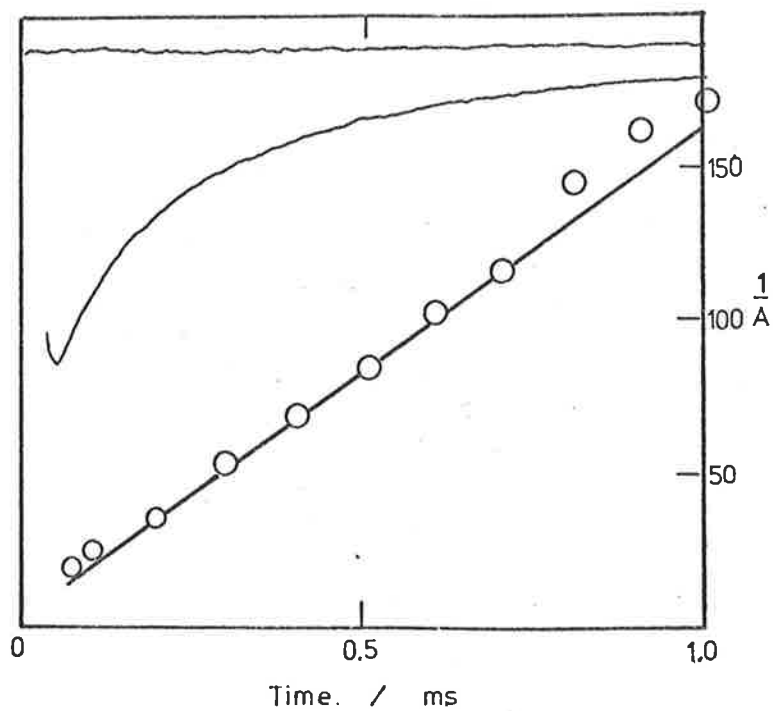
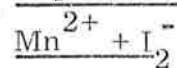


Fig. R13.3A



365 nm

$$2k = 7.3 \times 10^9$$

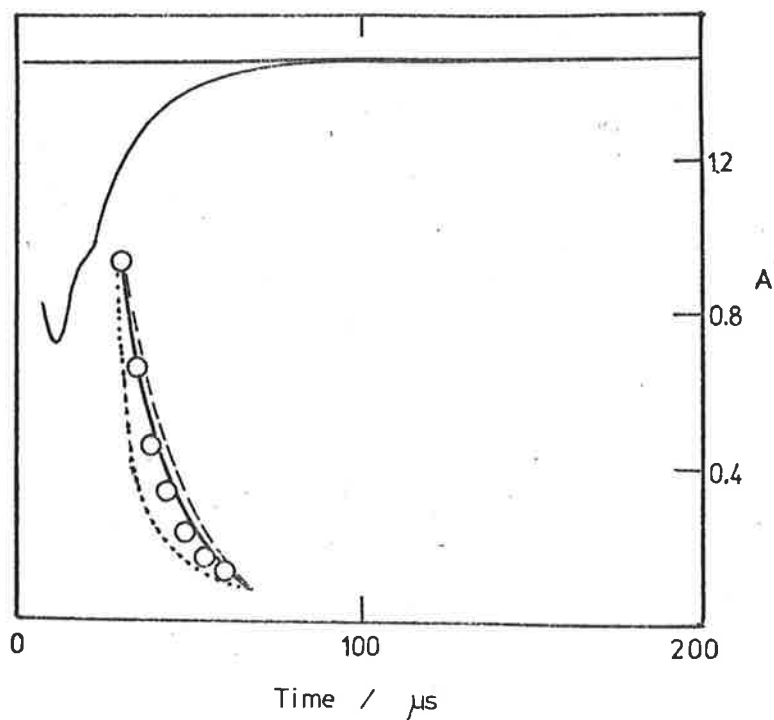
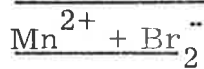


Fig. R13.3B



365 nm

.....2nd order

--- 1st order

— 1st + 2nd

○ Expt.

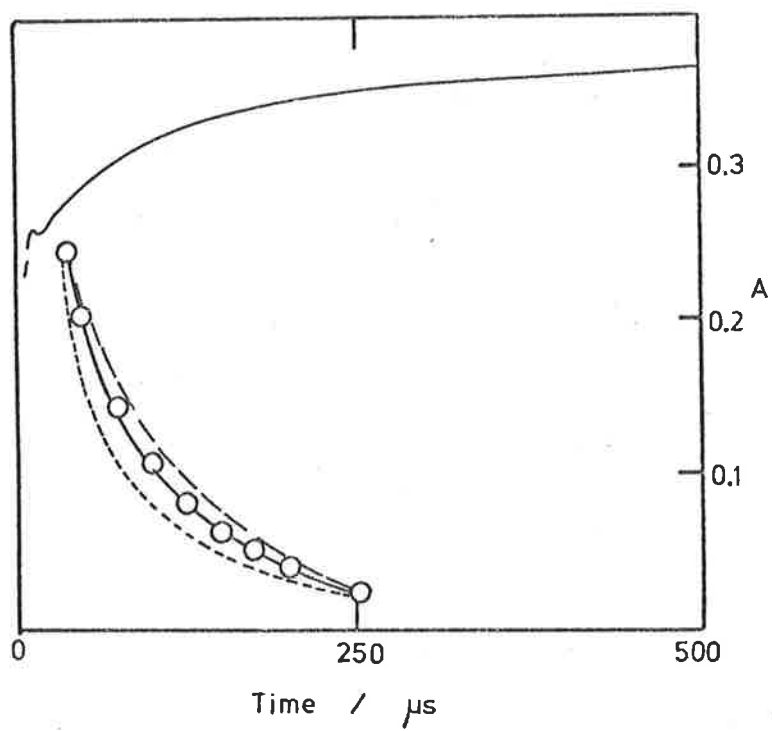
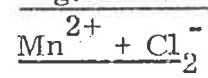


Fig. R13.3C



365 nm

.....2nd order

--1st order

—1st + 2nd

○ Expt.

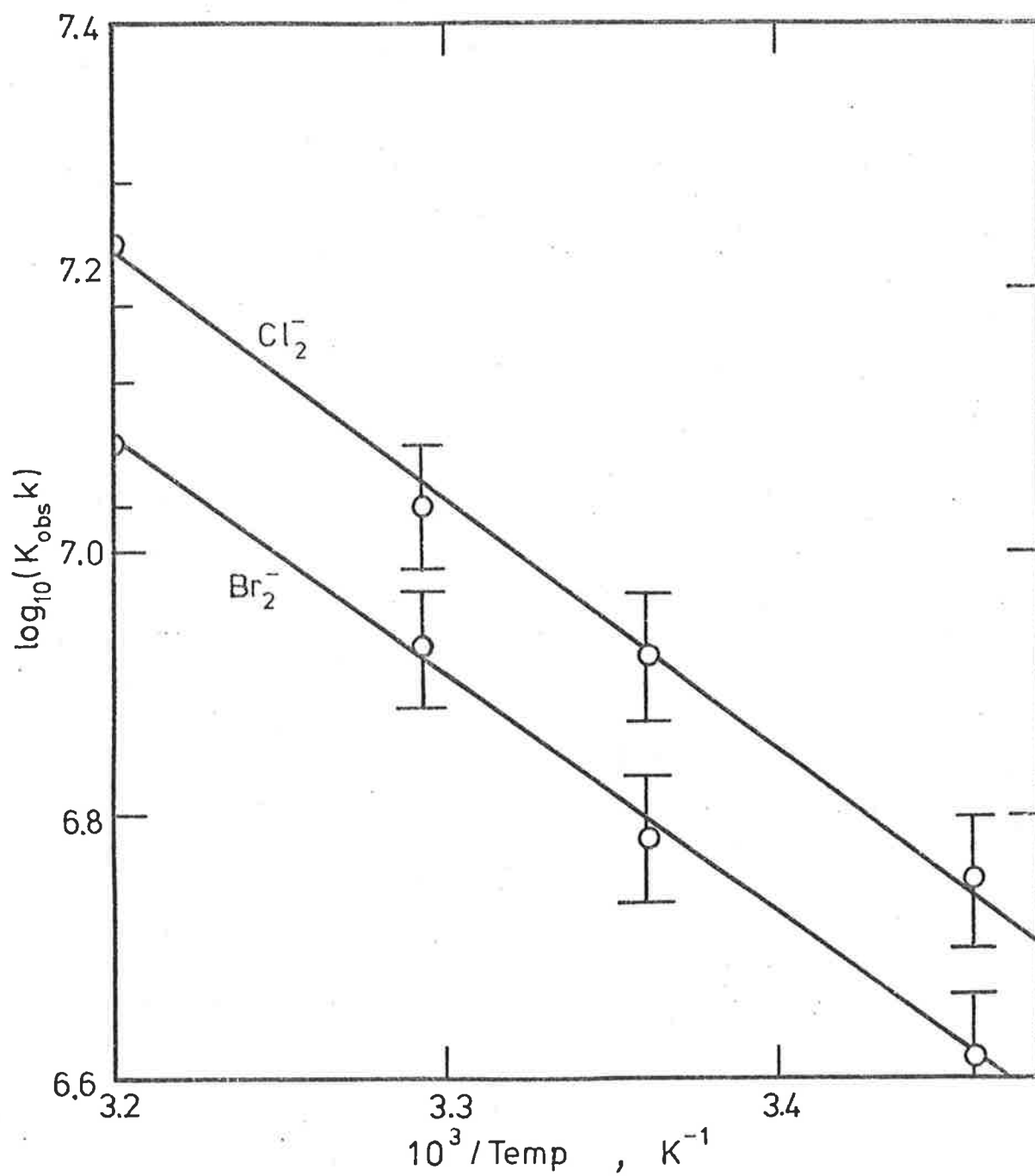


Fig. R13.3D Arrhenius Plots - $\text{Mn}^{2+} + \text{X}_2^-$

R13.4 NICKEL (II)R13.4.1 Br_2^- , I_2^-

In the presence of $0.05 \text{ mol l}^{-1} \text{ Ni}^{2+}_{\text{aq}}$ the decay of Br_2^- and I_2^- from halogen solutions was good second order. A typical oscilloscope trace and second order plot for Br_2^- is shown in Fig. R13.4A. The observed values of the second order rate constants are in excellent agreement with previously determined values for the disproportionation reactions ;

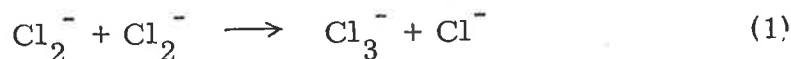
$$\text{Br}_2^- \text{ kobs} = (5.6 \pm 0.5) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1} \text{ (cf. } 5.3 \times 10^9 \text{)}$$

$$\text{I}_2^- \text{ kobs} = (7.4 \pm 0.8) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1} \text{ (cf. } 7.8 \times 10^9 \text{)}$$

The rate constant of any competing reaction of $\text{Ni}^{2+}_{\text{aq}}$ must be less than $2 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

R13.4.2 Cl_2^-

The rate of decay of Cl_2^- from a Cl_3^- solution is slightly increased by addition of $\text{Ni}^{2+}_{\text{aq}}$ in the range $10^{-2} - 7 \times 10^{-2} \text{ mol l}^{-1}$. The decay of Cl_2^- can be fitted by assuming a competitive second order disproportionation reaction



and pseudo first order reaction with metal ion.

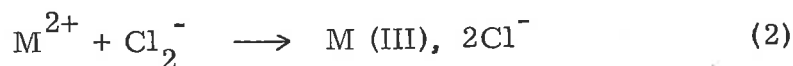


Fig. R13.4B shows a typical oscilloscope trace and fit of absorbance against time points by the computed first and second order decay.

Fig. R13.4.C shows the variation of the pseudo first order component with $[\text{Ni}^{2+}_{\text{aq}}]$. Derived rate constants are discussed in 13.4.2 and 13.4.4.

R13.4.3 OH

Fig. R13.4D shows the effect of $1.0 \text{ mol l}^{-1} \text{ Ni}^{2+}_{\text{aq}}$ on the rate of formation and yield of Cl_2^- in a pulse irradiated solution of Cl ($2 \times 10^{-3} \text{ mol l}^{-1}$) and acid ($4 \times 10^{-3} \text{ mol l}^{-1}$). Below 1.0 mol l^{-1} ,

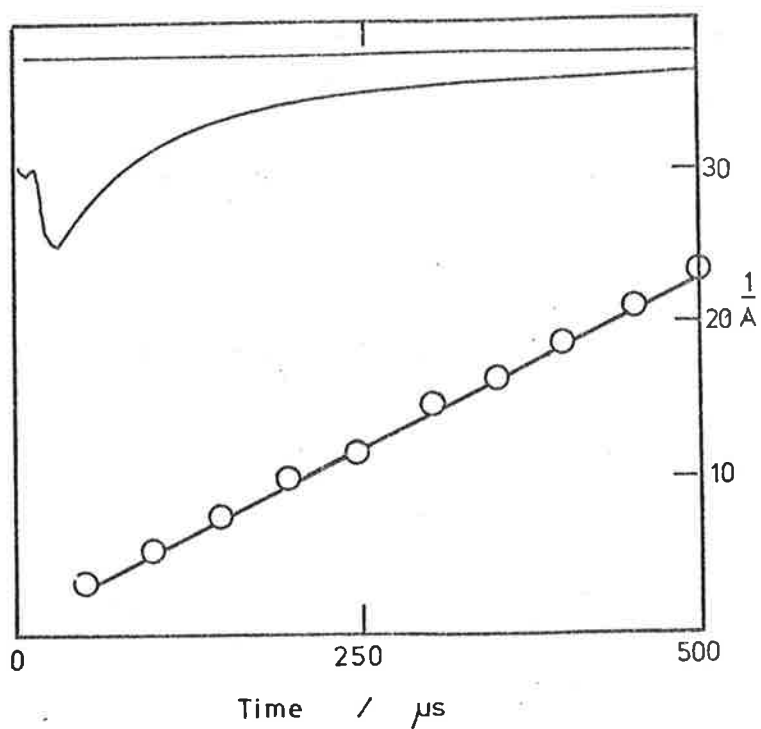
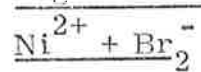


Fig. R13.4A



365 nm

$2k = 5.2 \times 10^9$

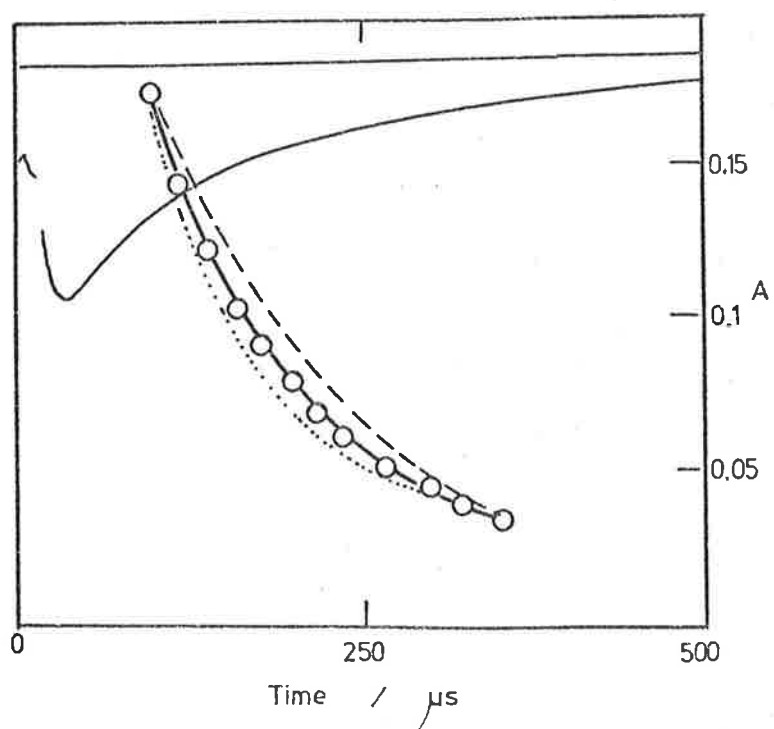
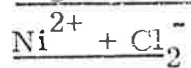


Fig. R13.4B



365 nm

.....2nd order

--1st order

—1st + 2nd

○ Expt.

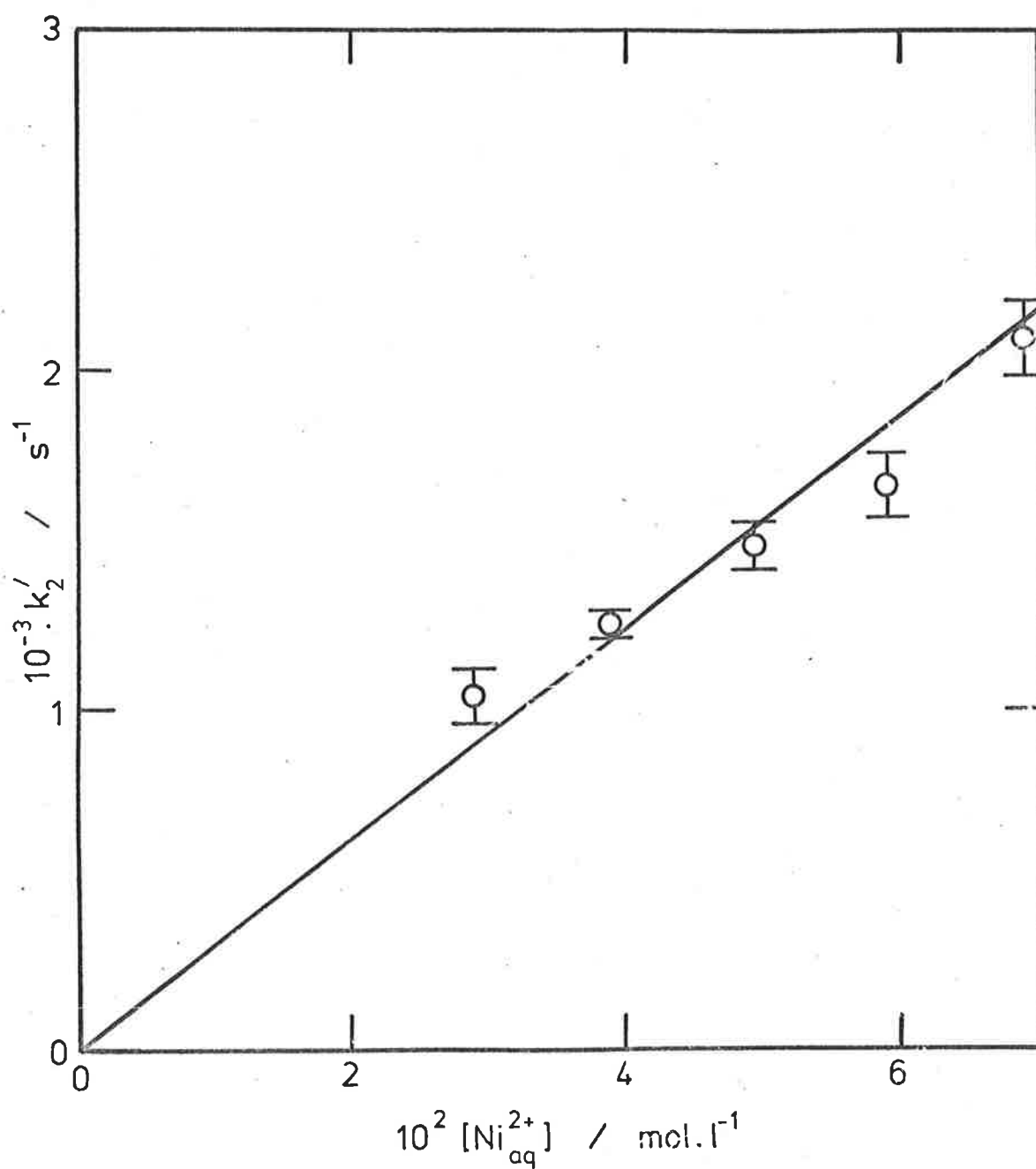
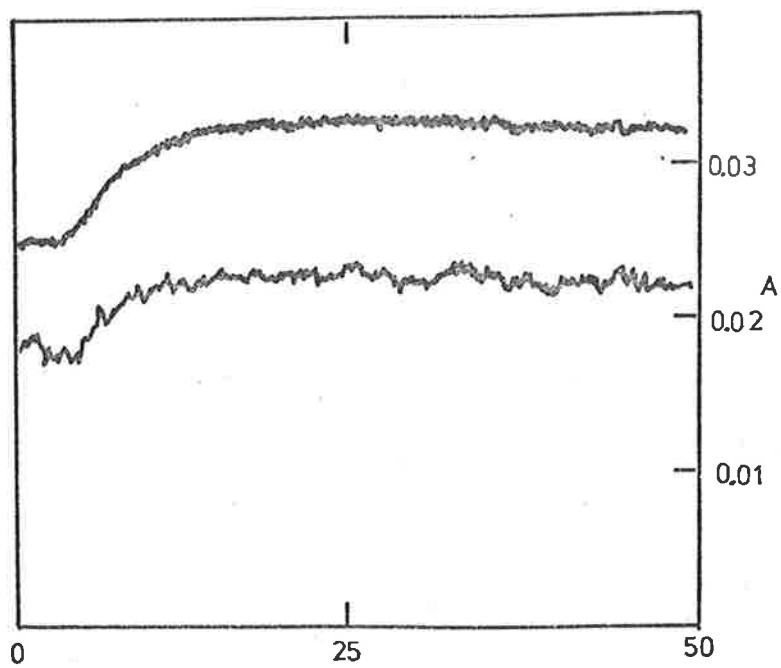


Fig. R13.4C $\text{Ni}^{2+}_{\text{aq}} + \text{Cl}_2^-$, Dependence of Pseudo First Order Rate Constant on $[\text{Ni}^{2+}_{\text{aq}}]$ at $22 \pm 2^\circ \text{C}$



FigR13.4D

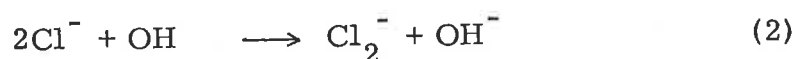
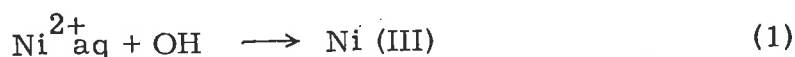
Ni²⁺ + OH

Competition - Cl⁻

350 nm

no effect of $\text{Ni}^{2+}_{\text{aq}}$ was observed.

Within the limits of experimental error the rate of formation of Cl_2^- is unaffected ($t_{1/2} \sim 3 \mu\text{s}$) but the yield of Cl_2^- drops by about 40%. The reduction in yield can be attributed to the competition of $\text{Ni}^{2+}_{\text{aq}}$ and Cl^- for OH radicals.



Reaction (2) is complex (See 4.5) and the true value of k_1 can only be roughly estimated from this observation. Impurities in the nickel perchlorate used, which at this concentration may also compete with chloride must also be considered. k_1 can be estimated as less than or of the order of $3 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

R13.5 COPPER (II)

R13.5.1 Cl_2^-

Fig. R13.5A shows a typical decay curve for Cl_2^- in the presence of $8 \times 10^{-2} \text{ mol l}^{-1} \text{ Cu}^{2+}_{\text{aq}}$, and the corresponding second order plot of $1/\text{absorbance}$ against time. The fit of the data to second order process is excellent and the observed rate constant of $(5.6 \pm 0.5) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ is in good agreement with that obtained in the absence of any reactive metal ions. (See Table 5.4A). The rate constant for reaction of $\text{Cu}^{2+}_{\text{aq}}$ with Cl_2^- is less than $2 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

R13.6 ZINC (II)

R13.6.1 Cl_2^- , Br_2^-

Fig. R13.6A shows a typical decay curve for Br_2^- in the presence of $5 \times 10^{-2} \text{ mol l}^{-1} \text{ Zn}^{2+}_{\text{aq}}$ and the corresponding plot of $1/\text{absorbance}$ against time. The fit of the data to a second order process is good and the observed rate constant of $(5.7 \pm 0.7) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ is in good agreement with that obtained in the absence of any reactive metal ion (See Table 5.3A). The rate constant for reaction of $\text{Zn}^{2+}_{\text{aq}}$ with

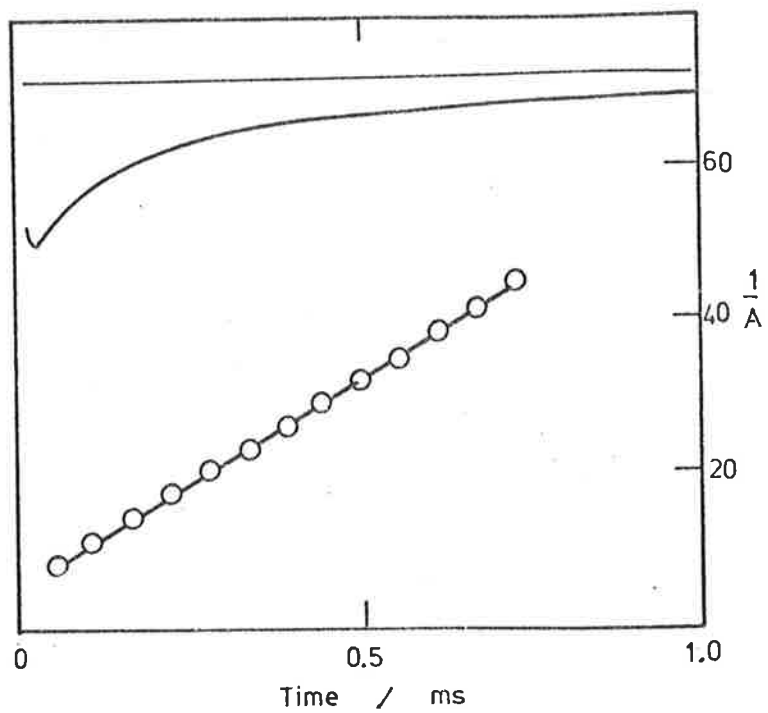
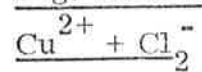


Fig. R13.5A



365 nm

$$2k = 5.6 \times 10^9$$

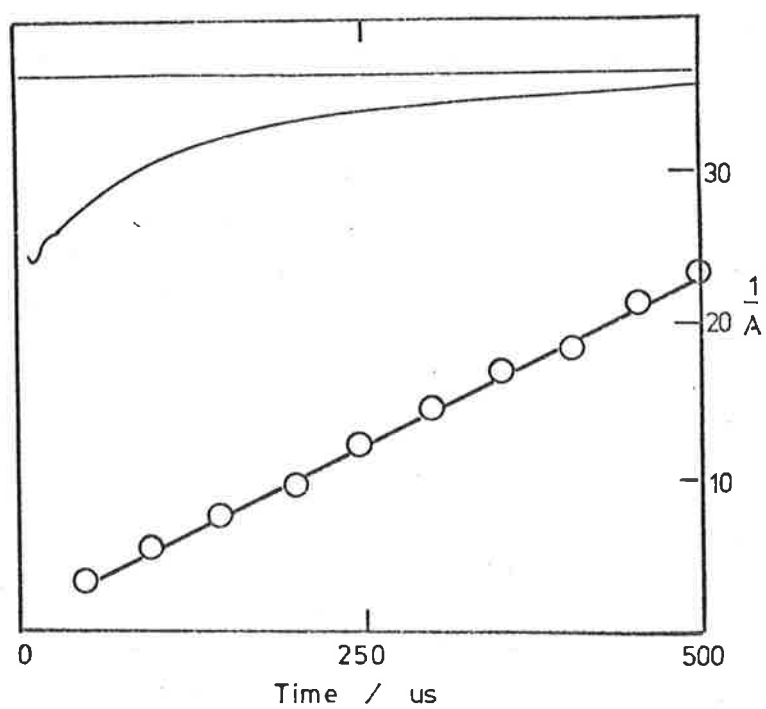
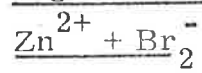


Fig. R13.6A



365 nm

$$2k = 5.3 \times 10^9$$

R25.

Br_2^- is $\leq 2 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

Similar results were obtained for Cl_2^- . The decay in the presence of $5 \times 10^{-2} \text{ mol l}^{-1} \text{ Zn}^{2+}_{\text{aq}}$ was excellent second order with a rate constant of $(5.8 \pm 0.6) \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ in good agreement with the value of $5.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ for the rate of disproportionation of Cl_2^- (See Table 5.4A). The rate constant for reaction of $\text{Zn}^{2+}_{\text{aq}}$ with Cl_2^- is $\leq 2 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$.

APPENDIX 1 - APPARATUS - TECHNICAL DETAILS

A1.1 FLASH PHOTOLYSIS APPARATUS

A general description of the flash photolysis apparatus has been given in Section 2.1.1. The theoretical and practical performance are discussed in 2.2 and 3.3. This appendix extends what was said in 2.1.1 and includes circuit details.

A1.1.1 Layout

Photograph 1 (see over page) shows the location of the major components of the flash photolysis apparatus. Photograph 2 shows a view of the flash lamp and cell within the aluminium reflector.

A1.1.2 Circuit details

Simplified versions of circuit diagrams for the flash production and detection systems are given in Figures A1.1A and A1.1B.

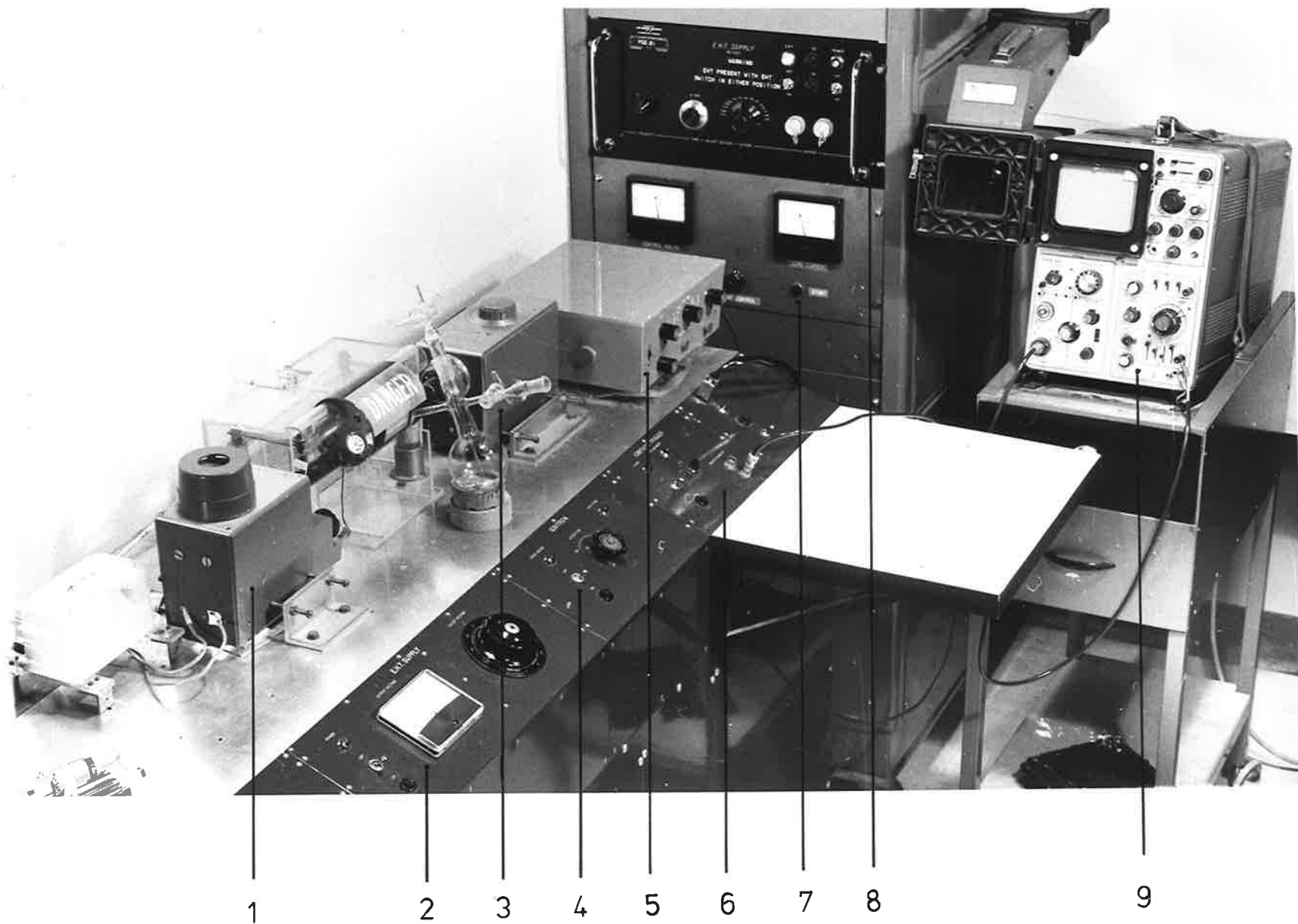
A1.1.3 Flash lamp - construction details

The construction of the flash lamp generally used is shown in Figure A1.1C. Some improvement in flash duration can be achieved by incorporation of a quartz capillary or rod with between 1 and 2 mm clearance inside the lamp. (Compare Hochanadel, Ghormley, Boyle and Riley, 1968; LeBlanc, Herbert, Whillans and Johns, 1972).

PHOTOGRAPH 1

Flash Photolysis Apparatus General View.

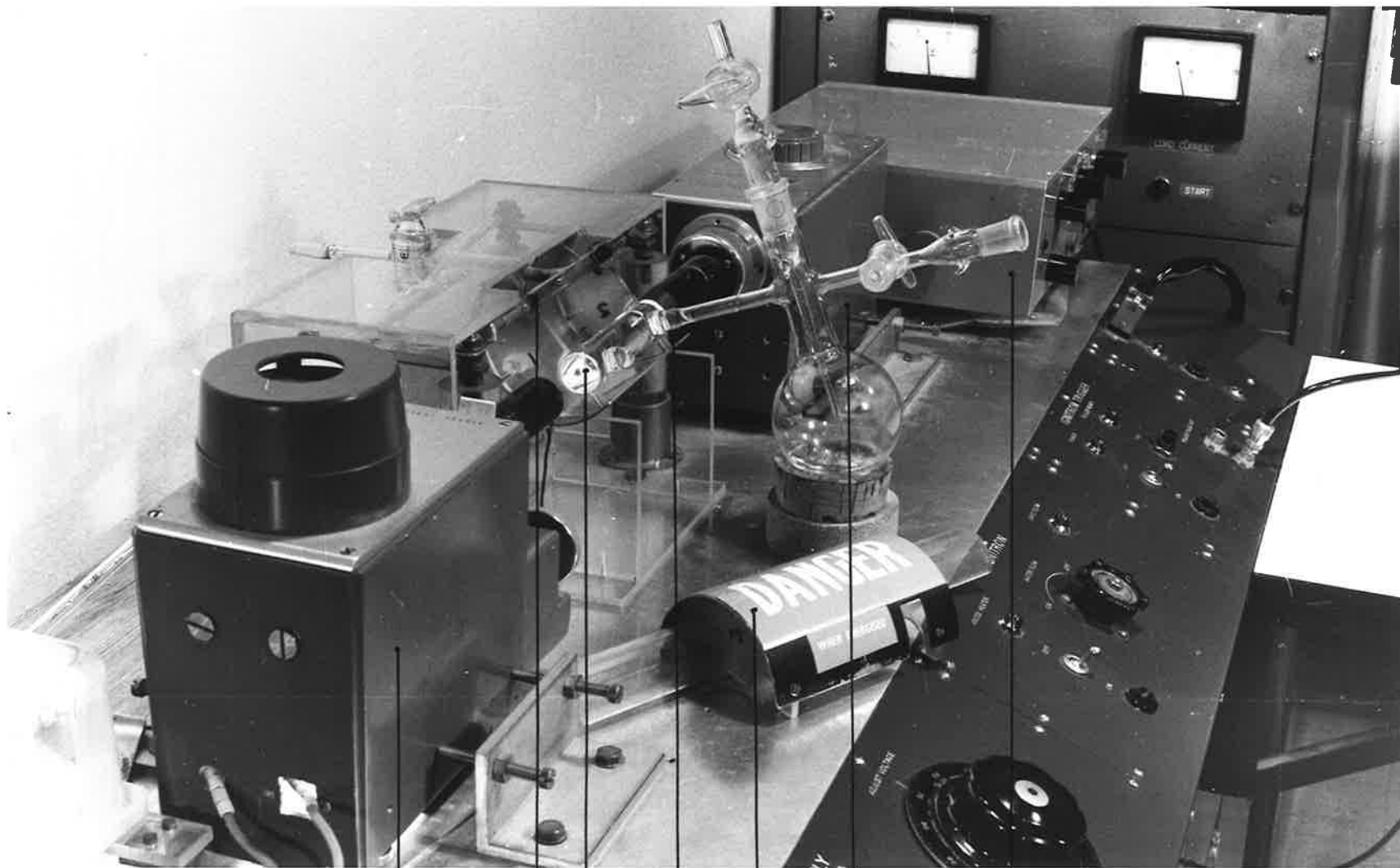
1. Monitoring lamp
2. Capacitor and power supply
3. Monochromator
4. Ignitron
5. Photomultiplier
6. Ignitron trigger
7. Monitoring lamp power supply
8. Photomultiplier power supply
9. Oscilloscope



PHOTOGRAPH 2

Flash Photolysis Apparatus - Flash Lamp and Cell.

1. Monitoring lamp
2. Flash lamp
3. Cell
- 4a. Reflector (bottom)
- 4b. Reflector (top)
5. Monochromator
6. Photomultiplier



1

2

3

4a

4b

5

6

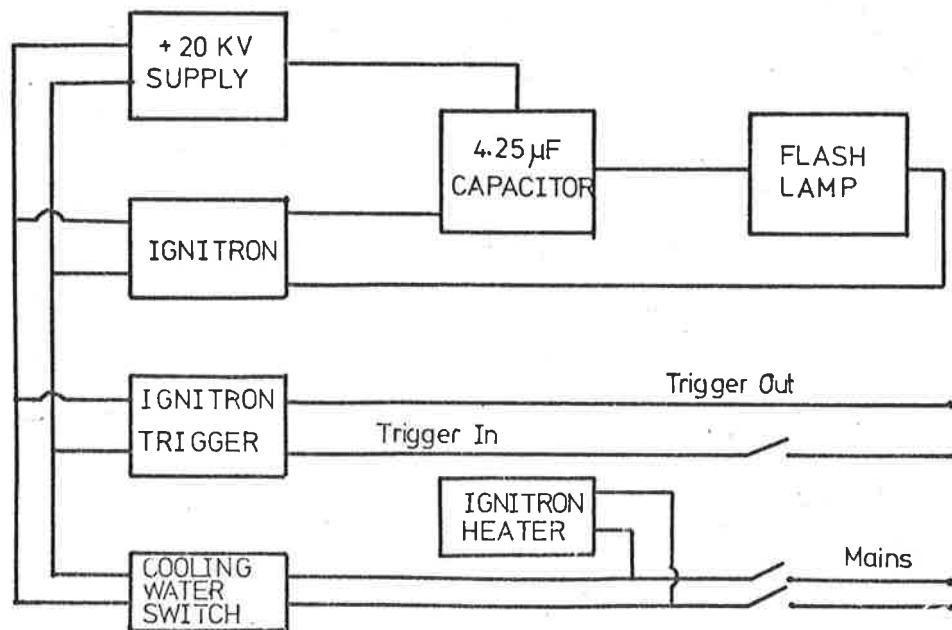


Fig. A1.1A Flash Production - Circuit Details

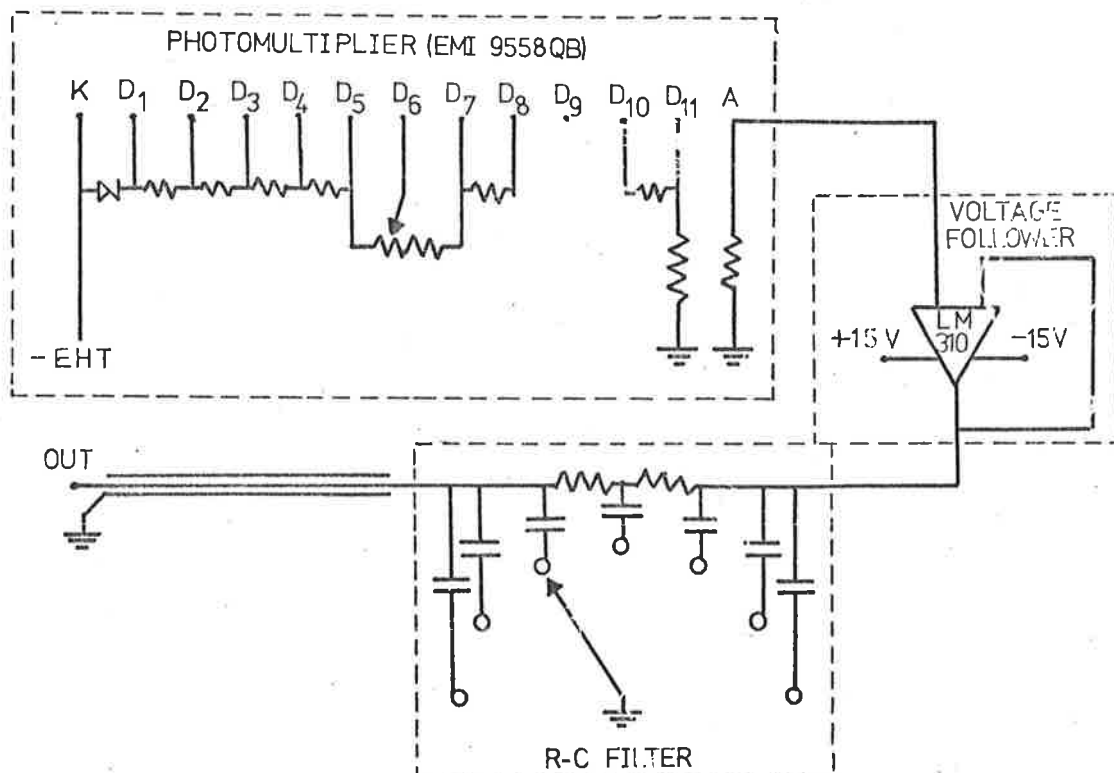


Fig. A1.1B Detection System - Circuit Details

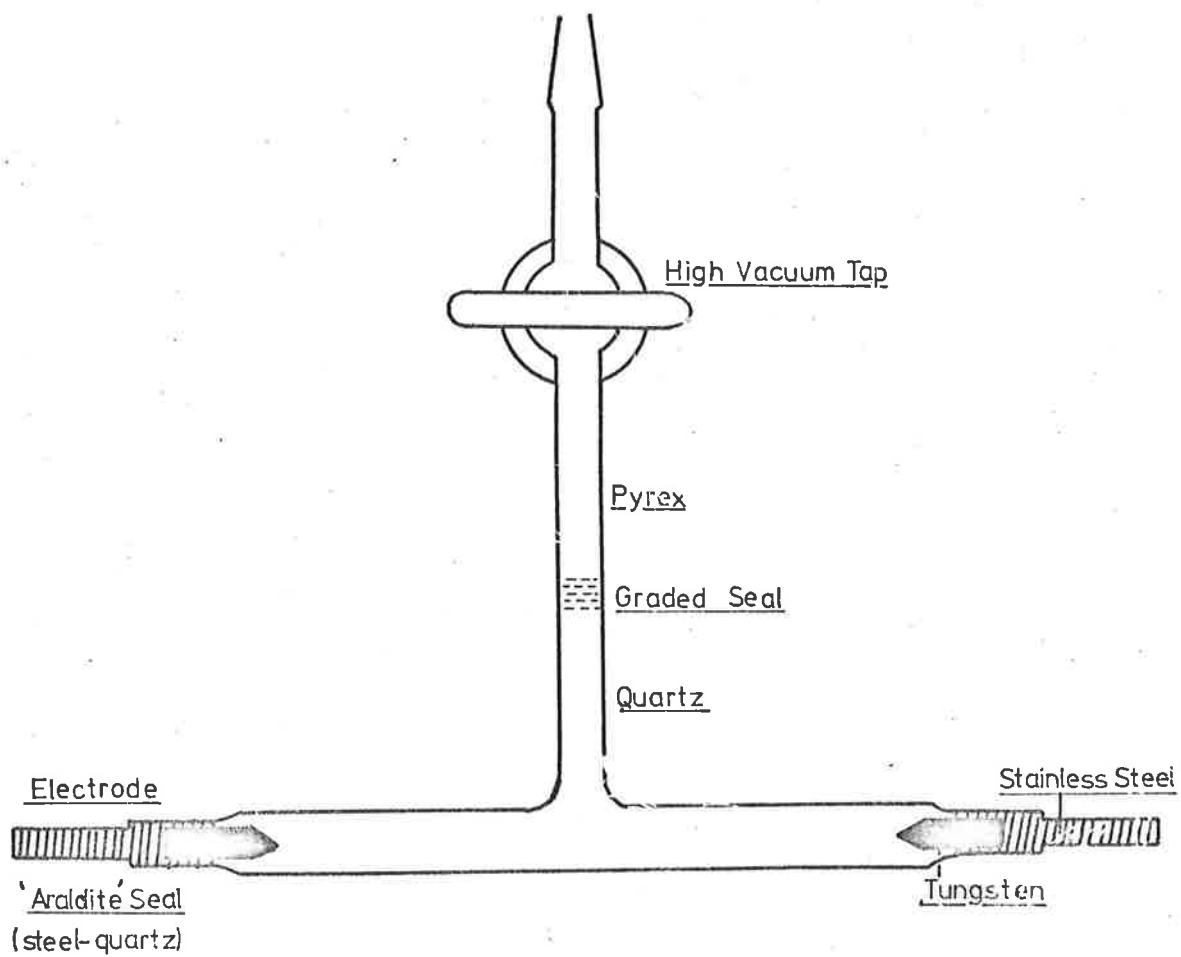


Fig. A1.1C Flash Lamp Construction

A1.2 TRACE READER

Figures A1.2A, A1.2B, A1.2C show the construction of the trace reader. Figure A1.2D gives the circuit details.

Key to Figures

- A - 3.5:1 reduction gear
- B - Pulleys
- C - Drum approx 1 cm (threaded)
- D - Helipot
- E - Tension adjust and clamping block
- F - Gain adjust potentiometer
- G - Zero adjust potentiometer
- H - Switches
- I - Perspex screen
- J - Helipot power supply
- K - Lamp power supply
- L - Fluorescent lamp
- M - Vernier calipers
- N - Transparent ruler
- P - Digital voltmeter

A1.2.1 Description

Rotation of the threaded drum (C) and helipot (D) through a reduction gear (A) causes a block (E) and ruler (N) attached to the movable portion of the vernier calipers (M) to move vertically up and down a photograph placed on the screen (I). The block is driven by multistranded steel wire of about 10 kg breaking strain. The tension in the wire is adjusted by two screws in the mounting block (E).

Application of an adjustable set voltage to the helipot allows a voltage, proportional to the position of the helipot and ruler to be read on a voltmeter (P). The voltage is read against an adjustable potential (G) which can be present to give zero output at a certain position.

Fig. A1.2A Trace Reader - Top View

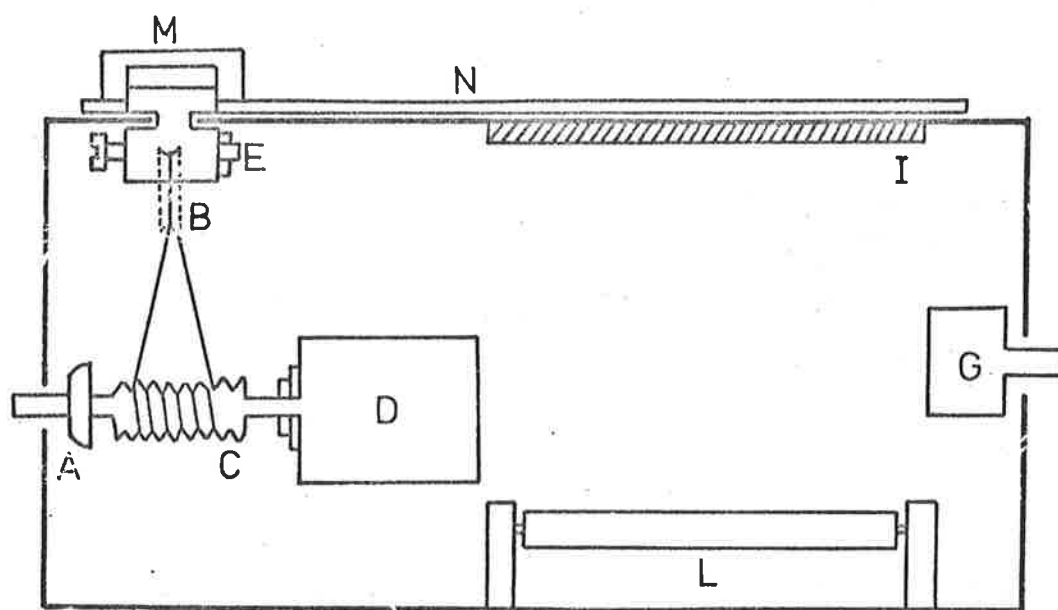
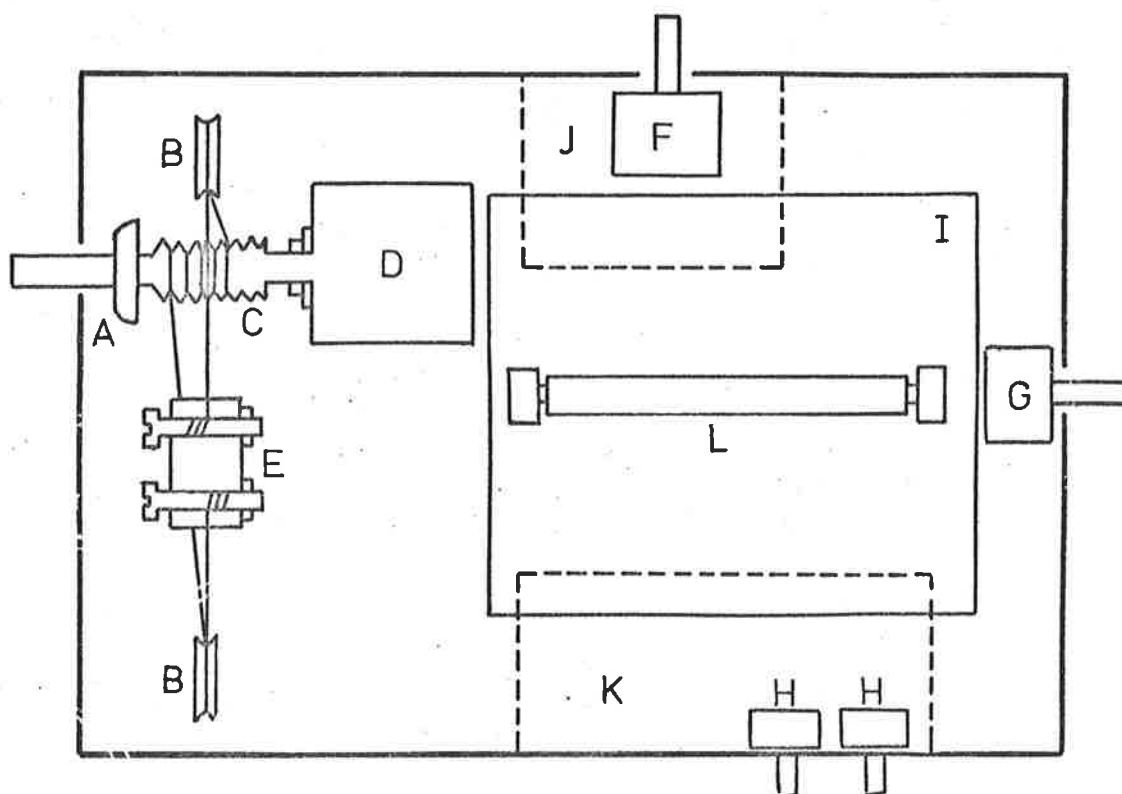


Fig. A1.2B Trace reader - Side View

Fig. A1.2C Trace Reader - End View

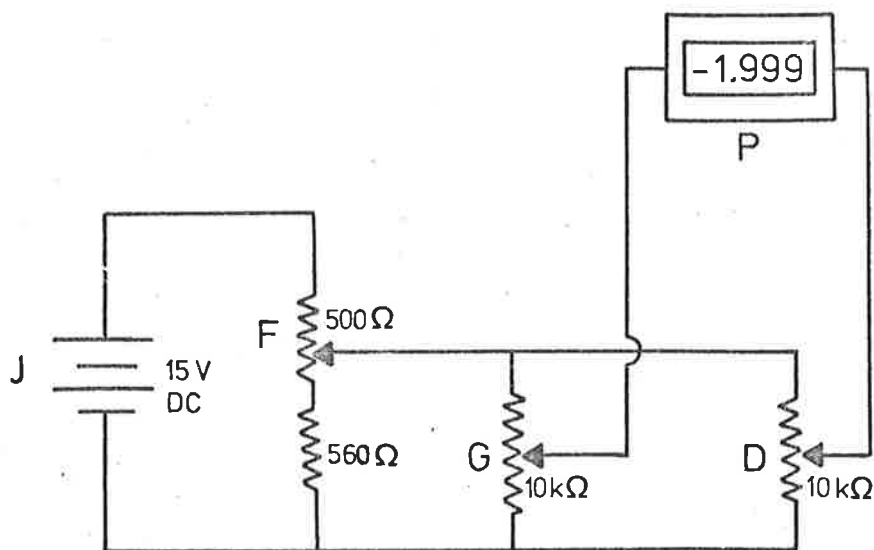
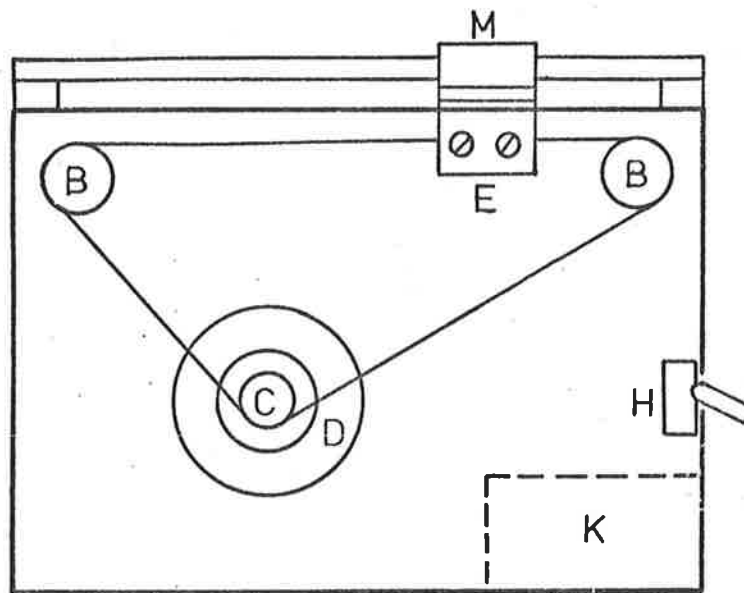


Fig. A1.2D Trace Reader - Circuit Details

APPENDIX 2 REDUCTION POTENTIALS

In Appendix 2 the reduction potentials of several radical reactions are calculated from kinetic and thermodynamic data. All thermodynamic data are quoted in kJ mol^{-1} and taken from Wagman, Evans, Parker, Halow, Bailey and Schumm. (1968)

A2.1 H ATOMS

A2.1.1 Calculation

$$\Delta G_f^\circ (\text{Hg}) = 203.8 \text{ kJ mol}^{-1}$$

$$\text{Now } \text{He}_g \rightleftharpoons \text{He}_{\text{aq}} \quad \Delta G_{\text{aq}} = +19.3 \text{ kJ mol}^{-1}$$

$$\text{Assume } \text{H}_g \rightleftharpoons \text{Haq} \quad \Delta G_{\text{aq}} = +19.3 \text{ kJ mol}^{-1}$$

$$\therefore \Delta G_f^\circ (\text{Haq}) = 223.1 \text{ kJ mol}^{-1}$$

$$\therefore \Delta G_f^\circ (\text{H}_{2g}) = 0 \text{ kJ mol}^{-1}$$

$$\Delta G_f^\circ (\text{H}_{2\text{aq}}) = 19.1 \text{ kJ mol}^{-1}$$

$$\text{Now } \text{Haq} \rightleftharpoons \frac{1}{2}\text{H}_{2\text{aq}}$$

$$\Delta G^\circ = \frac{1}{2}\Delta G_f^\circ (\text{H}_{2\text{aq}}) - \Delta G_f^\circ (\text{Haq})$$

$$= \frac{1}{2} (19.1 - 446.2) \text{ kJ mol}^{-1}$$

$$= -213.6 \text{ kJ mol}^{-1}$$

$$= 2.21\text{V}$$

$$\text{Now } \text{H}^+\text{aq} + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_{2\text{aq}} \quad 0.00 \text{ V}$$

$$\frac{1}{2}\text{H}_{2\text{aq}} \rightleftharpoons \text{Haq} \quad -2.21 \text{ V}$$

$$\text{H}^+\text{aq} + \text{e}^- \rightleftharpoons \text{Haq} \quad -2.21 \text{ V}$$

$$\text{And } \frac{1}{2}\text{H}_{2\text{aq}} + \text{e}^- \rightleftharpoons \text{H}^-\text{aq} \quad -2.23 \text{ V}$$

$$\text{Haq} \rightleftharpoons \frac{1}{2}\text{H}_{2\text{aq}} \quad +2.21 \text{ V}$$

$$\text{Haq} + \text{e}^- \rightleftharpoons \text{H}^-\text{aq} \quad -0.02 \text{ V}$$

A2.1.2 Literature comparison

The standard reduction potential

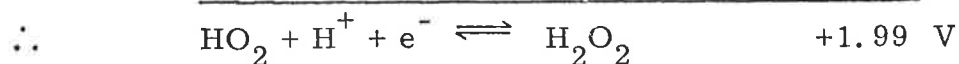
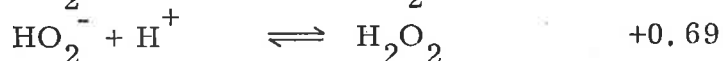
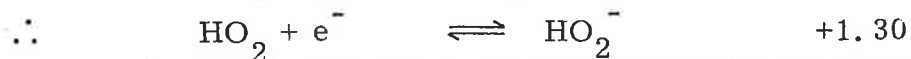
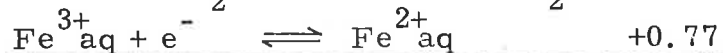
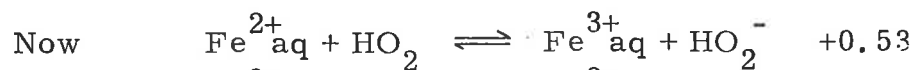
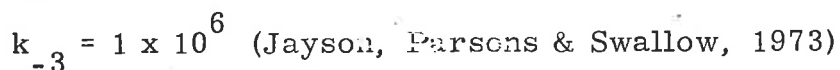
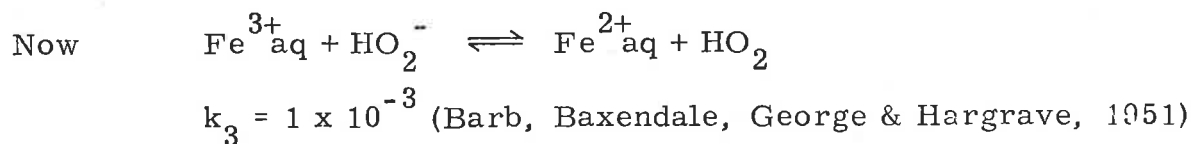
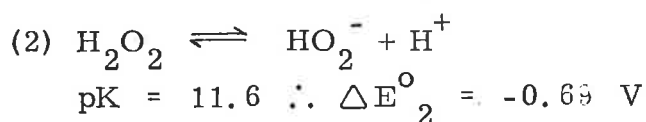
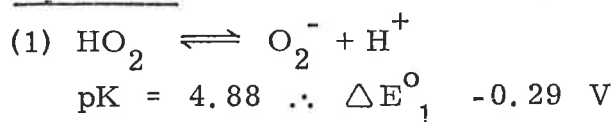


compares favourably with other estimates of -2.28 V (Navon & Meyerstein, 1970) and -2.30 V (Baxendale, 1964)

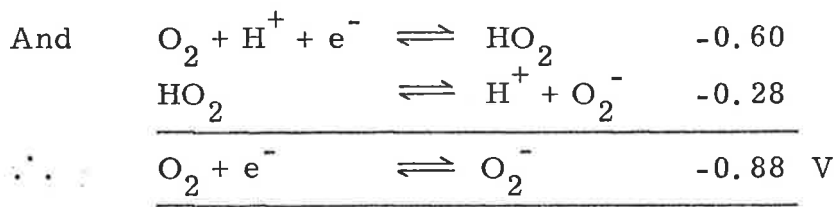
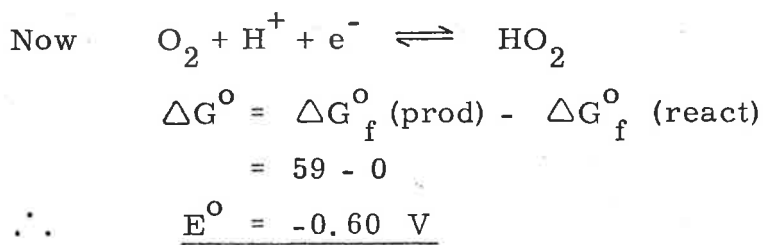
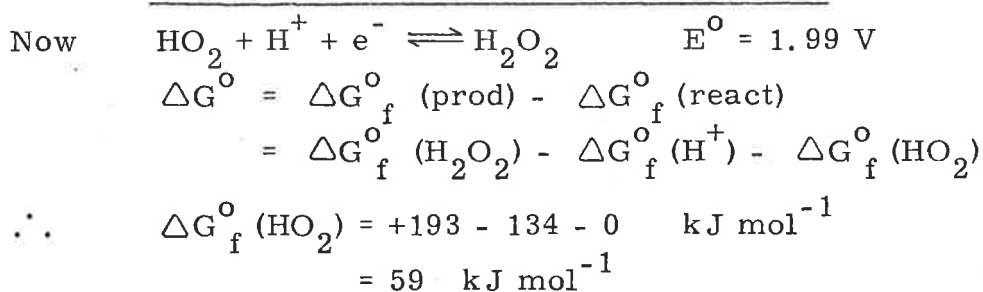
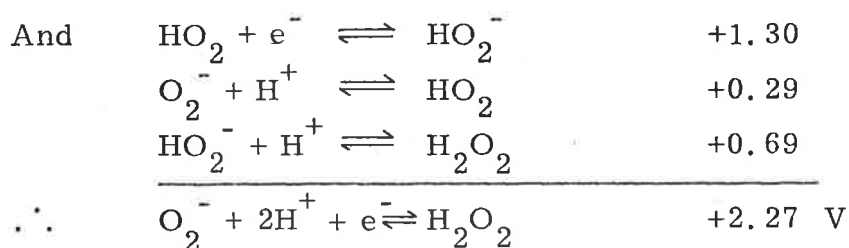
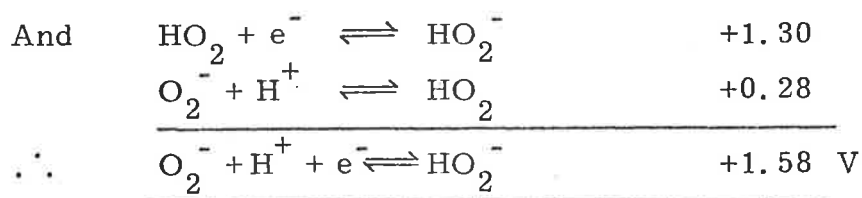
A2.2 PEROXY RADICALS

A2.2.1 Calculation

Equilibria



A5.



A2.2.2 Literature comparisons

Reaction	E°	Latimer ^a	Uri ^b
(1) $\text{H}^{+} + \text{O}_2 + \text{e}^{-} \rightleftharpoons \text{HO}_2$	-0.60	-0.1	
(2) $\text{O}_2 + \text{e}^{-} \rightleftharpoons \text{O}_2^{-}$	-0.88	-0.6	-0.6
(3) $\text{HO}_2 + \text{H}^{+} + \text{e}^{-} \rightleftharpoons \text{H}_2\text{O}_2$	+1.99	+1.5	+2.05
(4) $\text{O}_2^{-} + 2\text{H}^{+} + \text{e}^{-} \rightleftharpoons \text{H}_2\text{O}_2$	+2.27		
(5) $\text{O}_2^{-} + \text{H}^{+} + \text{e}^{-} \rightleftharpoons \text{HO}_2^{-}$	+1.58		
(1) + (3) $\text{O}_2 + 2\text{H}^{+} + 2\text{e}^{-} \rightleftharpoons \text{H}_2\text{O}$	+1.39	+1.36	

References:

(a) Latimer (1950)

(b) Uri (1952)

A7.

A2.3 HALOGEN RADICAL ANIONS

To calculate E° for halogen radical anions the following assumptions are necessary.

(a) Halogen radical anions are intermediates in the reduction of halogens to halides and oxidation of halides to halogens.

(b) $\Delta G_{\text{aq}}^{\circ}$ for X (i. e. $\text{Xg} \rightleftharpoons \text{Xaq}$)

is equal to $\Delta G_{\text{aq}}^{\circ}$ for nearest inert gas.

		Cl	Br	I	
$X_{2aq} + 2e^- \rightleftharpoons 2X^-_{aq}$	a	-264	-212	-103	kJ mol^{-1}
$Xg + e^- \rightleftharpoons X^-_{aq}$	b	x_1	x_2	x_3	kJ mol^{-1}
$Xaq \rightleftharpoons Xg$		-16	-15	-13.5	
$X_2^-_{aq} \rightleftharpoons Xaq \times X^-_{aq}$		+28.5	+30.5	+30	
$X_2^-_{aq} + e^- \rightleftharpoons 2X^-_{aq}$		$x_1 + 12.5$	$x_2 + 15.5$	$x_3 + 16.5$	kJ mol^{-1}
$Xaq + X^-_{aq} \rightleftharpoons X_2^-_{aq}$	c	-28.5	-30.5	-30	kJ mol^{-1}
$Xg \rightleftharpoons Xaq$	b	+16	+15	+13.5	kJ mol^{-1}
$Xg + e^- \rightleftharpoons X^-_{aq}$	d	x_1	x_2	x_3	kJ mol^{-1}
$X_{2g} \rightleftharpoons 2Xg$		+212	+162	+121.5	
$X_{2aq} \rightleftharpoons X_{2g}$		-7	-1	+3.5	
$X_{2aq} + e^- \rightleftharpoons X_{2aq}^-$		$x_1 + 182.5$	$x_2 + 145.5$	$x_3 + 108.5$	kJ mol^{-1}
$X_{2aq} + 2e^- \rightleftharpoons 2X^-_{aq}$		$2x_1 + 205$	$2x_2 + 161$	$2x_3 + 125$	kJ mol^{-1}
x		-235	-191	-114	kJ mol^{-1}

Summary	Cl	Br	I	
$X_2^- \text{aq} + e^- \rightleftharpoons 2X^- \text{aq}$	+2.29	+1.77	+1.00	V
$X_{2\text{aq}} + e^- \rightleftharpoons X^- \text{aq}$	+0.43	+0.41	+0.06	V
$X_{2\text{aq}} + 2e^- \rightleftharpoons 2X^- \text{aq}$	+2.72	+2.18	+1.06	V

Notes and References

- (a) Latimer (1950)
- (b) $\Delta G^\circ_{\text{aq}}$ nearest inert gas
- (c) $\Delta G^\circ = -RT \ln K$ (See Sections 4.4, 4.5, 4.6)
- (d) $\Delta G^\circ = 2 \Delta G^\circ_f (X_{\text{aq}}) - \Delta G^\circ_f (X_{2\text{g}})$
- (e) $\Delta G^\circ = \Delta G^\circ_f (X_{2\text{aq}}) - \Delta G^\circ_f (X_{2\text{g}})$

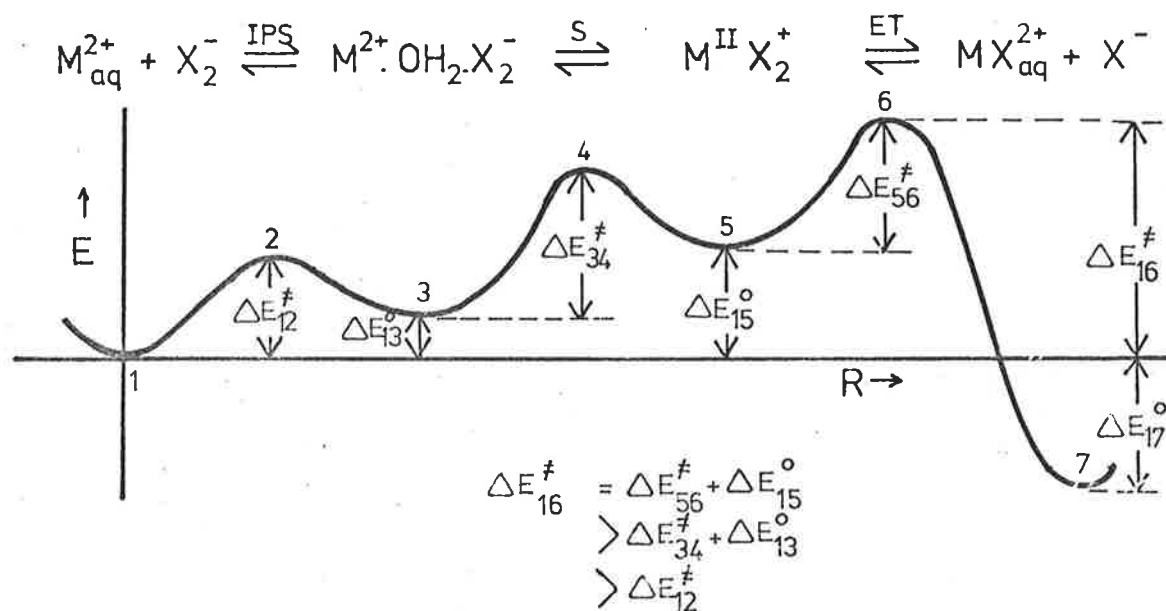
The derived values are compared with available literature values in Table 11.6A

APPENDIX 3 REACTION PROFILES

A reaction profile shows the change in an energy parameter E , which can be free energy G , or enthalpy H , as a function of a reaction coordinate which expresses the extent of reaction. Reactants, products and intermediates are represented as points of minimum energy. The points of maximum energy are transition states associated with the designated process. Inner sphere and outer sphere reactions will have different profiles and different steps within each of the mechanisms may be rate limiting depending upon which has the highest energy transition state. The energy of points beyond the highest transition state (i. e. after the rate limiting step) cannot be determined experimentally unless the reverse reaction can also be followed. The nature of the reaction profile after the high energy transition state is assumed.

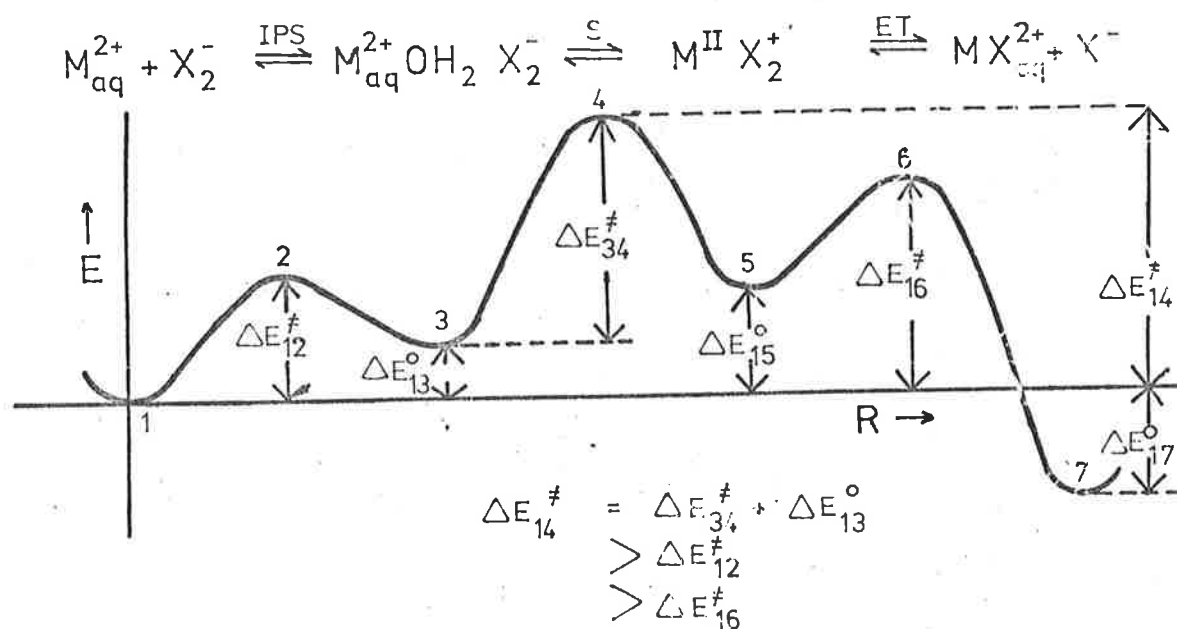
Reaction profiles have been drawn for all possible reaction mechanisms of halogen radical anions with divalent metal ions. For inner sphere reactions the electron transfer step may give a mono- or di-substituted oxidised complex; no experimental distinction between these cases has been possible, but it is assumed that the monosubstituted complex is formed directly. Substitution is assumed to follow the Eigen-Wilkins mechanism.

A3.1 INNER SPHERE ELECTRON TRANSFER CONTROLLED



e.g. $Mn_{aq}^{2+} + Br_2^-$, $Mn_{aq}^{2+} + Cl_2^-$

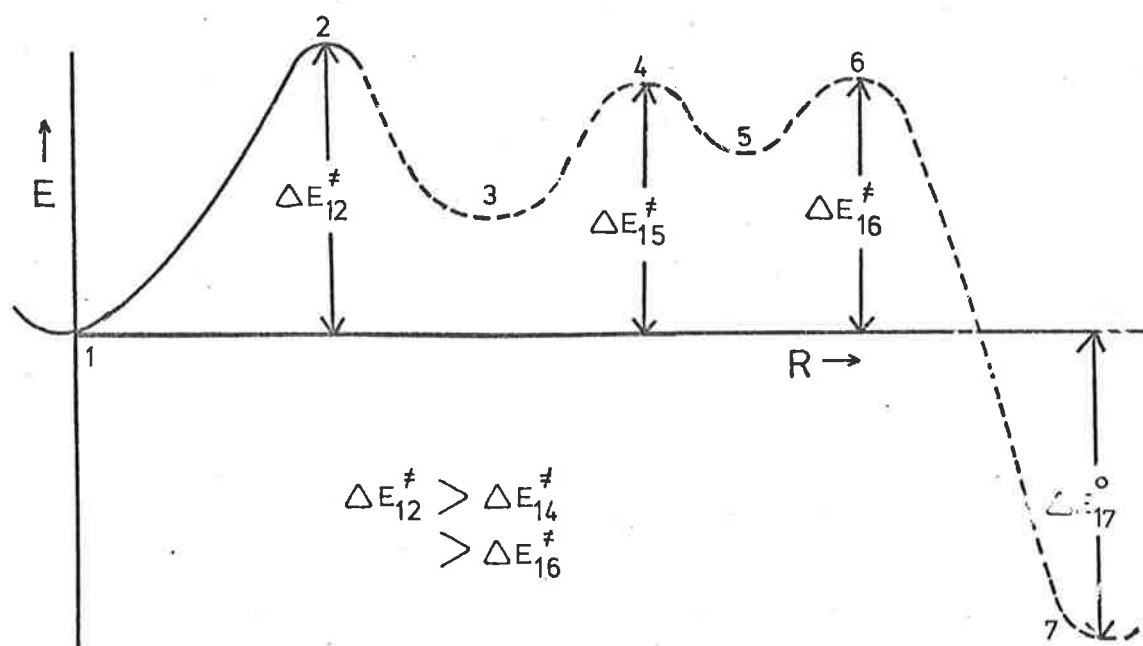
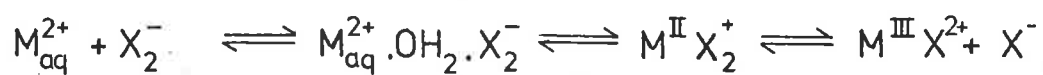
A3.2 INNER SPHERE SUBSTITUTION CONTROLLED



e.g. $Fe_{aq}^{2+} + Br_2^-$, $Fe_{aq}^{2+} + Cl_2^-$ (part), $Co_{aq}^{2+} + Cl_2^-$

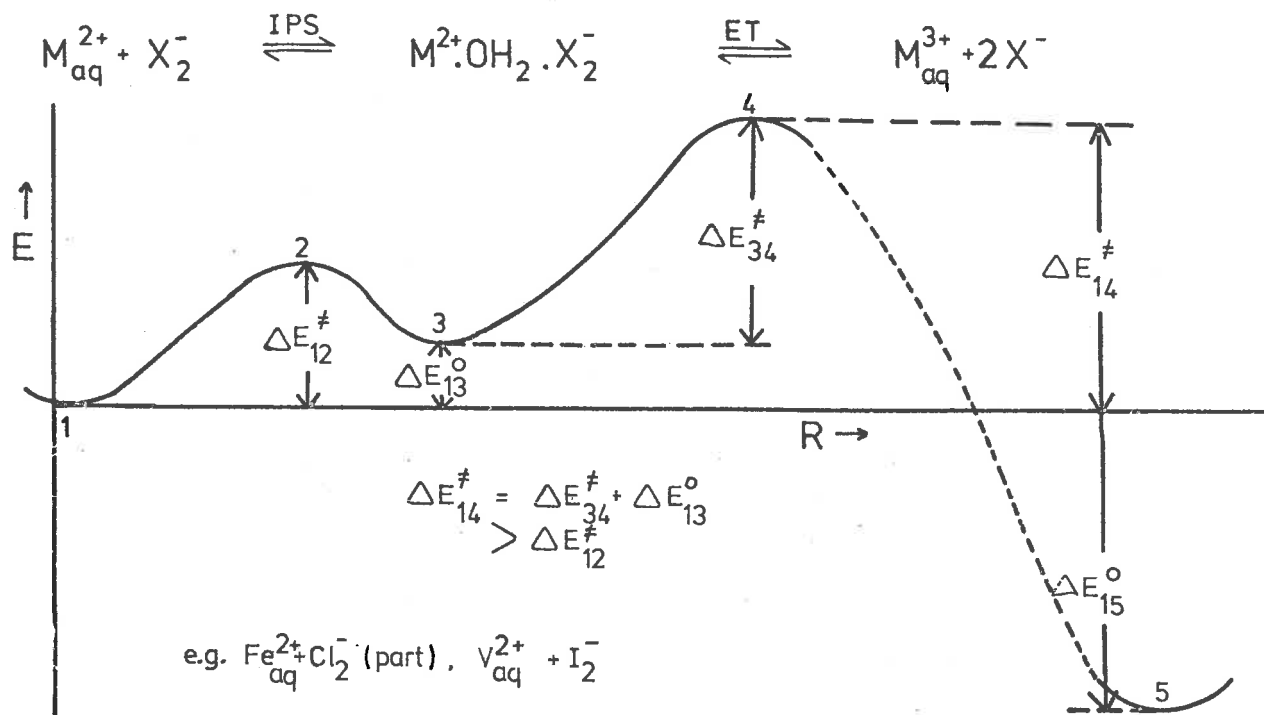
A12.

A.3.3 DIFFUSION CONTROLLED INNER SPHERE

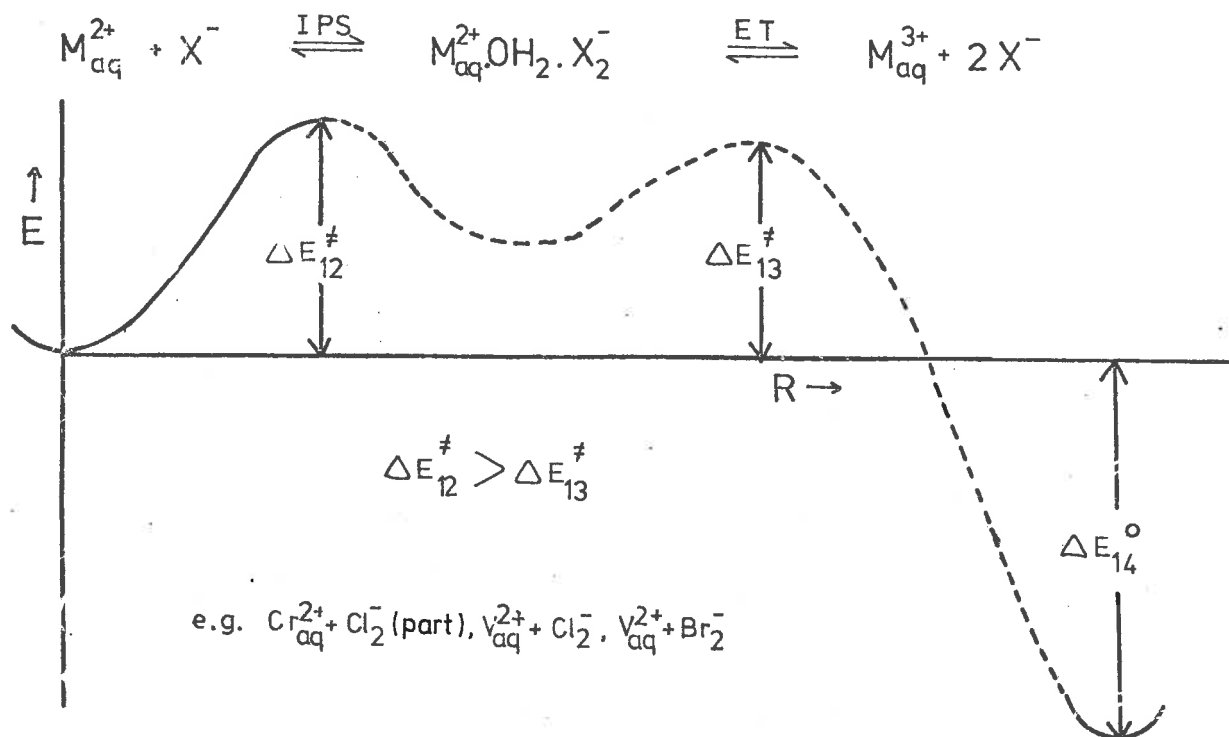


e.g. $Cr_{\text{aq}}^{2+} + I_2^-$, $Cr_{\text{aq}}^{2+} + Br_2^-$, $Cr_{\text{aq}}^{2+} + Cl_2^-$ (part)

A3.4 OUTER SPHERE



A3.5 DIFFUSION CONTROLLED OUTER SPHERE



APPENDIX 4 COMPUTER PROGRAMS

Computer programs were written for a CDC6400 computer using SCOPE 3.4. In Appendix 4 the programs are very briefly described and then listed. A sample out put is also given.

A4.1 PROGRAM EE

For a given incident light voltage, V_o , program EE calculates and tabulates optical density, $\log_{10}$ (optical density) and $1/(\text{optical density})$ increasing ΔV by 1 mV each time

$$OD = \log_{10} \frac{V_o}{V_o - \Delta V}$$

A4.2 PROGRAM A

Subroutine READER accepts y against x data, where y, the vertical deflection of the oscilloscope trace is related to ΔV by a magnification and scale factor, and x the horizontal distance from a given origin is related to time by the same magnification but different scale factor. V_o and an extinction coefficient are also read.

Program A calculates absorbances and finds the least squares best fit slopes of $\log_{10}$ (OD) and $1/(\text{OD})$. The accuracy of the fit is expressed by a correlation coefficient whose magnitude approaches 1 from below as the fit becomes better.

Subroutines SCALER and PLOTIT produce normalized first and second order plots of the data.

A4.3 PROGRAM FIT

Program fit calculates radical concentrations as a function of time using subroutine READER (see A4.2). With selected values of k_1 and k_2 it then calculates by a simple numerical integration procedure, the expected concentration against time curve starting from an experimentally extrapolated initial concentration.

$$-\frac{d[X]}{dt} = k_1[X] + k_2[X]^2$$

Three estimates of k_1 and one of k_2 are initially taken and the fit of the calculated and experimental points is compared. Over a small range of k_1 which should preferably span the true value, a plot of k_1 against the sum of the differences between experimental and calculated points is a straight line. The value of k_1 corresponding to a sum of the differences of zero is taken to be the best fit value. This value is subsequently used to calculate a fourth concentration against time curve.

A4.4 PROGRAM WR16

Program WR16 is our modification of WR16 by Schmidt (1966). The principles used to compute the concentration against time curves for up to 27 species and up to 30 reactions remain the same (see Schmidt, 1966). The program has been modified to plot some of the concentration against time curves. Central memory requirements have been minimized by use of storage discs and buffer statements and several other minor functions that were not directly available under SCOPE 3.4 have been replaced by equivalent functions.

The equilibrium routines designed to speed up execution time when rapid equilibria are involved have had READEQ, EQUIL 4 and COMP added to handle the situation of rapid coupled pre-equilibria.

Apart from the program list and sample output a sample set of data is included.

```

PROGRAM E(INPUT,OUTPUT)
REAL LD(5)
DIMENSION D(5),RD(5),V(5),IFORM(15)
V(5)=-0.001
LLT=10
V0=3.6
MM=4*V0
DO 3 M=1,MM
PRINT 11,V0
11  FORMAT(2H1 ,* V0 = *,F3.1,/)
PRINT 13
13  FORMAT(
$=====
$=====
$===*)
PRINT 15
PRINT 14
14  FORMAT(* : V : OD LOG OD 1/OD : V : OD LOG OD 1/OD :
$V : OD LOG OD 1/OD : V : OD LOG OD 1/OD : V : OD LO
$G OD 1/OD*)
PRINT 15
15  FORMAT(* : : : : : : :*)
$ : : : : : : :*)
PRINT 13
PRINT 15
PRINT 15
DO 1 I=1,50
V(1)=V(5)+0.001
D(1)=ALOG10(V0/(V0-V(1)))
IF(D(1).EQ.0.)GO TO 30
LD(1)=ALOG10(D(1))
GO TO 31
30  CONTINUE
LD(1)=0.
31  CONTINUE
RD(1)=1./D(1)
DO 2 N=2,5
V(N)=V(N-1)+0.001

```

```

      D(N)=ALOG10(V0/(V0-V(N)))
      LD(N)=ALOG10(D(N))
      RD(N)=1/D(N)
2      CONTINUE
      IF(D(1).NE.1.0)GO TO 40
      D(1)=1.0000001
40     IF(D(1).NE.0.)GO TO 41
      D(1)=10.**-10
41     LT=ALOG10(D(1)/10.**5)
      IF(LT.EQ.LLT)GO TO 4
      LLT=LT
      IF(D(1).GE.0.0001)GO TO 20
      IF=4 $ JF=0 $ GO TO 25
20     IF(D(1).GE.0.001)GO TO 21
      IF=4 $ JF=1 $ GO TO 25
21     IF(D(1).GE.0.01)GO TO 22
      IF=4 $ JF=2 $ GO TO 25
22     IF(D(1).GE.0.1)GO TO 23
      IF=4 $ JF=3 $ GO TO 25
23     IF(D(1).GE.1.0)GO TO 24
      IF=4 $ JF=4 $ GO TO 25
24     IF=3 $ JF=5
25     CONTINUE
      ENCODE(134,10,IFORM)IF,JF,IF,JF,IF,JF,IF,JF,IF,JF
10     FORMAT(20H(1X,*,*,F5.3,*,*,F6.,I1,7HF7.3F7.,I1,
$17H,*,*,F5.3,*,*,F6.,I1,7HF7.3F7.,I1,
$17H,*,*,F5.3,*,*,F6.,I1,7HF7.3F7.,I1,
$17H,*,*,F5.3,*,*,F6.,I1,7HF7.3F7.,I1,
$1H))
4      CONTINUE
      PRINT IFORM,(V(K),D(K),LD(K),RD(K),K=1,5)
1      CONTINUE
      PRINT 15
      PRINT 13
3      CONTINUE
      END E

```

```

C      PROGRAM A      (INPUT,OUTPUT)
C      A PRINTER PLOT MAY BE OBTAINED IF A FLAG IS NOT SET
C      PROGRAM OBTAINS FIRST AND SECOND ORDER PLOTS OF RATE DATA
C      DATA ARE X AND Y COORDINATES OF LIGHT INTENSITY VERSUS TIME
C      THE NUMBER OF POINTS, 100PERCENT LIGHT INTENSITY,AND SCALE
C      FACTORS ARE ALSO NEEDED. EXTINCTION COEFFICIENT MAY BE A DUMMY
      DIMENSION NAME(10),T(100),C(100),C1(100),C2(100)
      DIMENSION D(100)
      DIMENSION C3(50,2)
      COMMON/A1/E,TZ,TQD
9      READ 1,(NAME(I),I=1,8)
1      FORMAT(8A10)
      READ 2,N,NV,LOT
2      FORMAT(A1,I2,3X,A1)
      CALL READER(T,C,NV)
      DO 3 I=1,NV
        C1(I)=ALOG(C(I))
        C2(I)=1./C(I)
        D(I)=C(I)*E*10.
3      CONTINUE
      CALL LSQU(T,C1,NV,S1,R1,YI1,SERI1,PEI1,SERS1,PES1)
      CALL LSQU(T,C2,NV,S2,R2,YI2,SERI2,PEI2,SERS2,PES2)
      PRINT 4,(NAME(I),I=1,8)
4      FORMAT(1H1,10X,8A10,/////)
      PRINT 6
6      FORMAT(13X,*TIME                EXPT(CONC)                LN(CONC)                1/CO
      $NC                O.D.*,/)
      PRINT 5,(T(I),C(I),C1(I),C2(I),D(I),I=1,NV)
5      FORMAT(10X,E10.3,10X,E10.3,10X,2E10.3,10X,F8.5)
      PRINT 7,S1,R1,YI1
7      FORMAT(///,10X,*BEST 1ST ORDER K =*,E10.3,/,10X,*CORRELATION COEFF
      $ =*,F8.5,/,10X,*Y INTERCEPT =*,E10.3,///)
      PRINT 16
16     FORMAT (10X,*S.E.INTERCEPT*,10X,*P.E.INTERCEPT*,10X,*S.E.RATE CONS
      1TANT*,10X,*P.E.RATE CONSTANT*,/)
      PRINT 17, SERI1, PEI1, SERS1, PES1
17     FORMAT (/,12X,E9.2,16X,F5.2,18X,E9.2,20X,F5.2,/)
      PRINT 8,S2,R2,YI2

```

```

8      FORMAT(///,10X,*BEST 2ND ORDER K =*,E10.3,/,10X,*CORRELATION COEFF
$ =*,F8.5,/,10X,*Y INTERCEPT =*,E10.3,///)
      PRINT 16
      PRINT 17, SERI2, PEI2, SERS2, PES2
      IF(LOT.EQ.1H )GO TO 12
      CALL SCALE(C1,C2,C3,NV,FACT,T)
      PRINT 11,(NAME(I),I=1,2),FACT
11     FORMAT(/,10X,2A10,20X,*FIRST ORDER VALUES MADE POSITIVE AND MULTIP
SLIED BY*,F8)
12     CONTINUE
      IF(N.EQ.1H )GO TO 9
      STOP
      END A

```

```

      SUBROUTINE READER(T,C,NV)
      DIMENSION T(1),C(1),TI(100),V(100),VT(100)
      REAL MV,MT
      COMMON/A1/E,TZ,TQD
      READ 1,VPD,TPD,VO,MT,MV,N
1     FORMAT (F6.3,E10.1,2F6.3,F6.2,2X,A1)
      IF(N.NE.1H )2,3
2     READ 4,E
4     FORMAT(F5)
3     CONTINUE
      READ 5,(TI(I),V(I),I=1,NV)
5     FORMAT(16F5.2)
      VQD=VPD/MV
      TQD=TPD/MT
      TO=0.0
      DO 6 I=1,NV
      VT(I)=VO/(VO-VQD*V(I))
      C(I)=ALOG10(VT(I))/(E*10)
6     T(I)=TQD*TI(I)-TO
      RETURN
      END READER

```


A20.

2

```
SUBROUTINE LSQU(X,Y,N,S,R,YI,SERINT,PEI,SERS,PES)
DIMENSION X(100),Y(100)
XY=X2=Y2=CX=CY=0.
DO 2 I=1,N
  CX=CX+X(I)
  CY=CY+Y(I)
  XY=XY+X(I)*Y(I)
  X2=X2+X(I)*X(I)
  Y2=Y2+Y(I)*Y(I)
  XB=CX/N
  YB=CY/N
  SX=(X2/N-XB*XB)**0.5
  SY=(Y2/N-YB*YB)**0.5
  R=(XY/N-XB*YB)/(SX*SY)
  S=(R*SY)/SX
  YI=YB-S*XB
  SYY=Y2-CY*CY/N
  SXX=X2-CX*CX/N
  SERY=SQRT((SYY-S*S*SXX)/(N-2.0))
  SERS=SERY/SQRT(SXX)
  SERINT=SERY*SQRT(1.0/N+XB*XB/SXX)
  PCSE=(SERS/S)*100.0
  PES=ABS(PCSE)
  PEI=(SERINT*100.0)/YI
  PEI=ABS(PEI)
  RETURN
END LSQU
```

```
SUBROUTINE SCALE(C1,C2,C3,NV,FACT,T)
DIMENSION C10(50),C11(50),C1(50),C2(50),C3(NV,2),T(50)
DO 1 I=1,NV
```

```
DO 2 I=1,NV
C11(I)=C10(I)*FACT+YI
C3(I,1)=C11(I)
C3(I,2)=C2(I)
2  CONTINUE
CALL QIKPLT(T,C3,-NV,2,11H*TIME(SEC)*,9H*F(CONC)*)
RETURN
END SCALE
```

```

PROGRAM FIT
INTEGER TI(100)
DIMENSION Y1(100),Y2(100),C1(100),C2(100),ALN(100),RC(100)
DIMENSION Y(5)
DIMENSION SDIFF(5)
DIMENSION DIF(5)
COMMON/A/C(100),D(5,100),B(4),NV
DIMENSION CONC(100),R(100),T(100),NAME(10)
16 READ 15,(NAME(I),I=1,8)
15 FORMAT(8A10)
READ 1,N,NV,NP,A,(B(I),I=1,3)
1 FORMAT(I1,I2,I3,4X,4E10.3)
NVV=NV-1
IF(NP.LT.0)50,51
51 READ 2,(TI(I),I=1,NV)
2 FORMAT(20I4)
DO 12 I=1,NV
12 T(I)=TI(I)*.000001
READ 3,IE,(CONC(I),I=1,NV)
3 FORMAT(I1,/, (16F5.3))
DO 4 I=1,NV
4 C(I)=CONC(I)/10.**IE
GO TO 52
50 CALL READER(T,C,NV)
DO 53 I=1,NV
TI(I)=T(I)*1000000
53 CONTINUE
52 CONTINUE
NP=IABS(NP)
DO 5 J=1,4
DO 5 I=1,NV
D(J,I)=C(I)
5 CONTINUE
DO 6 J=1,3
40 CONTINUE
SDIFF(J)=0.
DIF(J)=0.
DO 7 K=1,NVV

```

```

      R(1)=D(J,K)
      DO 8 I=1,NP
      R(I+1)=-R(I)**2*A*(T(K+1)-T(K))/NP+R(I)*B(J)*(T(K+1)-T(K))/NP+R(I)
8      CONTINUE
      D(J,K+1)=R(NP+1)
      DIFF=D(J,K+1)/C(K+1)-1
      SDIFF(J)=SDIFF(J)+DIFF*DIFF
      DIF(J)=DIF(J)+DIFF
7      CONTINUE
6      CONTINUE
      IF(J.EQ.4)GO TO 42
      PRINT 14,(NAME(I),I=1,8)
14     FORMAT(1H1,10X,8A10,/)
      PRINT 9,A
9      FORMAT(30X,*COMPETING REACTIONS*,//,30X,*-DX/DT=A(X)2+BX*,//,20X,
1*A=2ND ORDER RATE CONSTANT = *,E10.3,/,20X,*B=1ST ORDER RATE CONST
1ANT = VARIABLE *,////)
      DO 30 I=1,NV
      Y1(I)=ALOG(C(I))
30     Y2(I)=1/C(I)
      CALL LSQU(T,Y1,NV,AK1,R1,YI,SERINT,PEI,SERS,PES)
      AAK1=-AK1
      CALL LSQU(T,Y2,NV,AK2,R2,YI,SERINT,PEI,SERS,PES)
      C1(1)=C(1)
      C2(1)=C(1)
      ALN(1)=ALOG(C(1))
      RC(1)=1/C(1)
      SDIFF1=SDIFF2=0.
      DIF1=DIF2=0.
      DO 31 I=2,NV
      ALN(I)=ALN(1)+AK1*(T(I)-T(1))
      RC(I)=RC(1)+AK2*(T(I)-T(1))
      C1(I)=EXP(ALN(I))
      C2(I)=1/RC(I)
      DIFF1=C1(I)/C(I)-1
      DIFF2=C2(I)/C(I)-1
      SDIFF1=SDIFF1+DIFF1*DIFF1
      SDIFF2=SDIFF2+DIFF2*DIFF2

```

```

DIF1=DIF1+DIFF1
DIF2=DIF2+DIFF2
31 CONTINUE
CALL LSQU(B,DIF,3,S,R,YI,SERINT,PEI,SERS,PES)
B(4)=-YI/S
J=4
GO TO 40
42 CONTINUE
PRINT 32,AAK1,R1,AK2,R2
32 FORMAT(10X,*RESULTS TREATED AS 1ST ORDER GIVE*,/,15X,*RATE CONSTAN
1T = *,E10.3,/,15X,*CORRELATION COEFF = *,F7.5,/,10X,*RESULTS TREA
2TED AS 2ND ORDER GIVE*,/,15X,*RATE CONSTANT = *,E10.3,/,15X,*CORRE
3LATION COEFF = *,F7.5,////)
PRINT 43,B(4)
43 FORMAT(10X,*BEST VALUE OF B TO FIT ABOVE RATE LAW = *,E10.3,////)
PRINT 33,(B(I),I=1,4)
33 FORMAT(1X,*TIME(USEC)      EXPERIMENTAL      BEST 1ST      BEST 2
1ND      B1=*,E10.3,5X,*B2=*,E10.3,5X,*B3=*,E10.3,5X,*B4=*,E10.
23,/)
DO 35 I=1,NV
35 PRINT 34,TI(I),C(I),C1(I),C2(I),(D(J,I),J=1,4)
34 FORMAT(3X,I5,9X,E10.3,7X,E10.3,5X,E10.3,10X,E10.3,8X,E10.3,8X,E10.
13,8X,E10.3)
PRINT 37,DIF1,DIF2,(DIF(I),I=1,4)
37 FORMAT(///,1X,*SUM OF RESIDUALS*,17X,E10.3,5X,E10.3,10X,E10.3,8X,E
110.3,8X,E10.3,8X,E10.3)
PRINT 36,SDIFF1,SDIFF2,(SDIFF(I),I=1,4)
36 FORMAT(///,1X,*SUM OF SQUARES OF RESIDUALS*,6X,E10.3,5X,E10.3,10X,
1E10.3,8X,E10.3,8X,E10.3,8X,E10.3)
IF(N.EQ.0)GO TO 16
STOP
END FIT

```

```

SUBROUTINE LSQU(X,Y,N,S,R,YI,SERINT,PEI,SERS,PES)
DIMENSION X(100),Y(100)
XY=X2=Y2=CX=CY=0.
DO 2 I=1,N
CX=CX+X(I)
CY=CY+Y(I)
XY=XY+X(I)*Y(I)
X2=X2+X(I)*X(I)
2 Y2=Y2+Y(I)*Y(I)
XB=CX/N
YB=CY/N
SX=(X2/N-XB*XB)**0.5
SY=(Y2/N-YB*YB)**0.5
R=(XY/N-XB*YB)/(SX*SY)
S=(R*SY)/SX
YI=YB-S*XB
SYY=Y2-CY*CY/N
SXX=X2-CX*CX/N
SERY=SQRT((SYY-S*S*SXX)/(N-2.0))
SERS=SERY/SQRT(SXX)
SERINT=SERY*SQRT(1.0/N+XB*XB/SXX)
PCSE=(SERS/S)*100.0
PES=ABS(PCSE)
PEI=(SERINT*100.0)/YI
PEI=ABS(PEI)
RETURN
END LSQU

```

PROGRAM WR16 (INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=
1PUNCH,TAPE10)

C
INTEGER A,AC,AE,AN,AAC,AAN
INTEGER B,BLANK,CALL,CHARGE,CHEM
INTEGER P,SPSK

C
DIMENSION A(31,6),AAC(6),AAN(6),AM(4,5),AN(30),B(31,6),CCL(1500)
DIMENSION CP(6),CSK(2,31),DCDT(30,20),DR(31),G(28),IEQ(31)
DIMENSION NRS(5,31),PROD(30),S(28),SPSK(2,31),T(31)

C
EQUIVALENCE (CC(1),CCL(1))

C
COMMON CC(30,50),CONCN(500,5),KOEFF(27,30),KOEFL(27,30),
1 ODCOND(500)

C
COMMON/BLOCK1/ AC(30),C(30),CHARGE(28),NC

C
COMMON /BLOCK2/ IFAIL

C
COMMON /BLOCK3/ NEQ

C
COMMON /BLOCK5/ DELTA

C
COMMON /BLOCK6/ ABSI,CONDI,DTP,EQCO(28),EXT(28),LT,
1INC1,NC2,NC3,NPR,TIME,TT(250),LTT

C
COMMON /BLOCK7/ DT

C
COMMON /BLOCK8/ ISK(30),ISK3(30),JSK(30),JSK3(30),
1 M1(30),M2(30),NR,RF(27),RK(31)

C
COMMON /BLOCK9/ DTPL0T,III,NRI(2),NPRINT,POTIME(500)

C
COMMON /BLOCK10/ MPL0T,NBUFO,PTT(30),XC(10)

C
COMMON /BLOCK11/ CI(30),MEQA

```

COMMON /BLOCK12/ CALL,L
C
DATA (BLANK=5H      ),(MINUS=1H-),(DELTA=2.5E-06),(P=5),
1  (AM=1.5,1.916666667,2.291666667,2.640277778,-0.5,-1.333333333,
2  -2.458333333,-3.852777778,0.,0.416666667,1.541666667,
3  3.633333333,0.,0.,-0.375,-1.769444444,3(0.),0.348611111)
C
C
C
C
C  READ RUN NUMBER (NORUN) AND PUNCH INDEX (IPUNCH)
C
C  MLOT=0
1  READ(5,200)NORUN,IPUNCH
C
C
C  PRINT DATE AND TEST FOR EOF ON INPUT DATA
C
C  DAY=DATE(DDATE)
C  WRITE(6,999)
C  IF(E0F(5))600,2
2  WRITE(6,300)NORUN,DAY
C
C  READ PLOTTING PARAMETERS
C
C  PTT REFERENCES THE SPECIES TO BE PLOTTED BY COLUMN NUMBER
C  0 FOR NO PLOT, 1 FOR PLOT
C  TO PLOT CONDUCTANCE, 1 IN COLUMN 28
C  TO PLOT OPTICAL DENSITY, 1 IN COLUMN 29
C  NRI REFERENCES THE TWO SPECIES WHOSE RATIO IS TO BE PLOTTED
C  SPECIES NUMBERS IN COLUMNS 31-32 AND 33-34
C  PLTMIN REFERENCES THE MINIMUM PLOT INTERVAL TIMES IN SECONDS
C  PLTMIN AS E10.3 IN COLUMNS 41-50
C
C  READ(5,210)(PTT(I),I=1,30),(NRI(I),I=1,2),PLTMIN
210  FORMAT(30F1.0,2I2,6X,E10.3)
C  NCOUNT=0
C  LLOT=0
1012  NCOUNT=NCOUNT+1
C  IF(PTT(NCOUNT).EQ.0)GO TO 1011

```



```

      LPLOT=1
      GO TO 1013
1011  CONTINUE
      IF(NCOUNT.LT.30)GO TO 1012
1013  CONTINUE
      NPRINT=0
      III=0
      DO 1010 I=1,10
1010  XC(I)=0.0
C
C      READ, COUNT, AND PRINT CHEMICAL REACTIONS
C
      DO 5 I=1,31
      II=I
      READ(5,201)(A(I,K),K=1,3),(B(I,K),A(I,K),K=4,6),RK(I)
      IF (A(I,1) - BLANK) 5,6,5
      5 WRITE(6,301)(A(I,K),K=1,3),(B(I,K),A(I,K),K=4,6),I,RK(I)
      6 NR=II-1
      IF (NR.EQ.0) NR=1
      7 CONTINUE
C
C      READ, COUNT AND PRINT SPECIES ETC.
C
      WRITE(6,302)
      DO 10 J=1,28
      JJ=J
      READ(5,203)CHARGE(J),AC(J),G(J),S(J),CI(J),EQCO(J),EXT(J)
      IF(CHARGE(J).EQ.0) CALL SCAN(CHARGE(J),AC(J))
      IF(AC(J)-BLANK)10,11,10
      10 WRITE(6,303)J,CHARGE(J),AC(J),G(J),S(J),CI(J),EQCO(J),EXT(J)
      11 NC=JJ-1
C
C      DEFINE SOME VALUES
C
      NC1=NC+1
      NC2=NC+2
      NC3=NC+3
      DO 12 J=NC1,30

```

```

12 CI(J)=0.
C
C   COMPUTE AND PRINT INITIAL CONDUCTIVITY AND OPTICAL DENSITY
C
  CONDI=0.
  ABSI=0.
  DO 100 M=1,NC
    CONDI=CONDI+CI(M)*EQCO(M)*ABS (FLOAT (CHARGE(M)))*0.001
100 ABSI=ABSI+CI(M)*EXT(M)
    WRITE(6,400)CONDI,ABSI
C
C   READ, COUNT AND PRINT DOSE RATE VALUES
C
  WRITE(6,304)
  DO 15 K=1,31
    KK=K
    READ(5,205)T(K),DR(K),SPSK(1,K),SPSK(2,K),CSK(1,K),CSK(2,K),(NRS(M
1,K),M=1,5),IEQ(K)
    IF(IEQ(K).EQ.0.AND.T(K).GT.00.)NT1=MAX0(1,K)
    IF(T(K))15,19,15
15 WRITE(6,305) K,T(K),DR(K),SPSK(1,K),SPSK(2,K),CSK(1,K),CSK(2,K),
1(NRS(M,K),M=1,5),IEQ(K)
19 NT=KK-1
C
C   READ OR DEFINE AND PRINT, SOME PARAMETERS FOR COMPUTATION
C
  READ(5,206)ACCFAC,NP,DTPMIN,DTMIN,DTMAX,DTMXEQ,IFR
  IF(ACCFAC.LE.0.)ACCFAC=0.05
  IF(DTPMIN.LE.0..AND.NP.LE.1)NP=250
  IF(DTMIN.LE.0.)DTMIN=T(NT1)/1000000.
  IF(DTMAX.LE.0.)DTMAX=T(NT1)/200.
  IF(DTMXEQ.LE.0.)DTMXEQ=T(NT1)/10000.
C
C   SET MAIN PROGRAM COUNTERS
C
  CALL=0
  MEQA=0

```

```

      CALL READEQ
      WRITE(6,306)ACCFAC,NP,DTPMIN,DTMIN,DTMAX,DTMXEQ
      IF(IFR.NE.0)WRITE(6,307)
      WRITE(6,308)
C
C      READ AND PRINT EQUILIBRIUM EQUATIONS
C
      IFAIL=0
      CALL EQUIL1
      IF(IFAIL)425,425,535
535 WRITE(6,666)
      GO TO 1
425 CONTINUE
C
C      CALCULATE COEFFICIENTS OF DIFFERENTIAL EQUATIONS
C
      CALL PLOTST(NPLOTS,NPTS)
      DO 30 I=1,NR
      ISK(I)=0
      ISK3(I)=0
      DO 30 J=1,NC
      KOEFF(J,I)=0
      KOEFL(J,I)=0
      IF(AC(J)-A(I,1)) 23,22,23
22 KOEFF(J,I)=KOEFL(J,I)-1
      M1(I)=J
23 IF(AC(J)-A(I,2))25,24,25
24 KOEFF(J,I)=KOEFL(J,I)-1
      M2(I)=J
25 KOEFL(J,I)=KOEFL(J,I)
      DO 30 K=3,6
      IF(AC(J)-A(I,K))30,26,30
26 KOEFF(J,I)=KOEFL(J,I)+1
      IF(B(I,K)-MINUS)30,27,30
27 KOEFF(J,I)=KOEFL(J,I)-2
30 CONTINUE
C
C      INITIALIZE

```

C

```
DO 50 J=1,30
C(J)=CI(J)
JSK(J)=0
JSK3(J)=0
50 CC(J,1)=CI(J)
TIME = 0.
DT=DTMIN
LT=0
LTT=0
REWIND 10
NBUFO=0
NRUFI=0
CALL STORE
IF (IFAIL) 53,53,535
53 CONTINUE
MEQ=0
```

C

C START SOLVING DIFFERENTIAL EQUATIONS

C

```
DO 120 IT=1,NT
```

C

C SKIPPING PROCEDURE

C

```
DO 450 M=1,2
IF (SPSK(M,IT)-BLANK) 431,450,431
431 DO 435 J=1,NC
IF (SPSK(M,IT)-AC(J)) 435,432,435
432 JSK(J)=JSK(J)+1
IF (IEQ(IT).GE.2) JSK3(J)=JSK(J)
IF (IEQ(IT).LT.2) C(J)=CSK(M,IT)
GO TO 450
435 CONTINUE
450 CONTINUE
DO 470 M=1,5
IF (NRS(M,IT)) 470,470,455
455 I=NRS(M,IT)
ISK(I)=ISK(I)+1
```

```

      IF (MEQ.GE.2) ISK3(I)=ISK(I)
470  CONTINUE
      MEQ=MAX0(MEQ,IEQ(IT))
      IF (TIME-T(IT))34,120,120
C
C      END OF SKIPPING ROUTINE
C
34  DO 35 L=1,NC
35  RF(L)=S(L)+(DR(IT)*G(L))/6.0231E+25
      LCYCL=0
      ILINK=0
      IF (DT.GE.(2.*DTMIN))DT=DT*0.5
36  DO 65 NCYCL=1,20
      LCYCL=MIN0(LCYCL+1,P)
C
C      START CYCLE OF COMPUTTAUION
C
      TIME =TIME+DT
      DO 51 I=1,NR
      IF (ISK(I))52,52,51
52  N1=M1(I)
      N2=M2(I)
      PROD(I)=C(N1)*C(N2)*RK(I)
51  CONTINUE
      DO 60 L=1,NC
      IF (JSK(L))43,43,6000
43  DCDT(L,NCYCL)=RF(L)
C
C      MAIN PROGRAM BRANCHES TO EQUILIBRIA
C
      IF (MEQA.EQ.0)GO TO 501
      IF ((L-MEQA).GE.0.AND.(L-MEQA).LE.2)CALL EQUIL4
501  CONTINUE
      DO 42 I=1,NR
      IF (ISK(I))44,44,42
44  IF (KOEFF(L,I)) 41,42,41
41  DCDT(L,NCYCL)=DCDT(L,NCYCL)+PROD(I)*FLOAT (KOEFF(L,I))
42  CONTINUE

```

```

      SLOPE=0.
      IF(ILINK)54,54,58
C
C      STANDARD ROUTINE FOR COMPUTING SLOPE
C
      54 IF(LCYCL-1)55,55,56
      55 SLOPE=DCDT(L,NCYCL)
         GO TO 59
      56 DO 57 K=1,LCYCL
         INDK=NCYCL+20+1-K-20*((NCYCL+20-K)/20)
      57 SLOPE=SLOPE+AM(LCYCL-1,K)*DCDT(L,INDK)
         GO TO 59
C
C      *LINK* ROUTINE FOR COMPUTING SLOPE
C
      58 IDIF=-1
         DO 158 K=1,P
            ISTEP=1
            IF((K+ILINK).GT.(P+1))ISTEP=2
            IDIF=IDIF+ISTEP
            INDK=NCYCL+20-IDIF-20*((NCYCL+20-IDIF-1)/20)
      158 SLOPE=SLOPE+AM(P-1,K)*DCDT(L,INDK)
C
C      CALCULATE AND STORE NEW CONCENTRATIONS
C
      59 IF(TIME.LT.T(IT))159,258
      258 C(L)=C(L)+SLOPE*(DT+T(IT)-TIME)
         GO TO 6000
      159 C(L)=C(L)+DT*SLOPE
      6000 CONTINUE
      60 CONTINUE
C
C      STORE VALUES FOR PLOTTING IF REQUIRED
C
      IF(LPLOT.EQ.0.OR.NPRINT.NE.0)GO TO 1015
      IF (TIME.LT.T(IT)) 1018,1017
      1018 DTPLOT=DTPLOT + DT
         GO TO 1019

```

```

1017 DTPLOT=DTPLOT + DT + T(IT) - TIME
1019 IF(III.GE.501)GO TO 1014
      IF(DTPLOT.GE.PLTMIN)CALL PLOTST(NPLOTS,NPTS)
      GO TO 1015
1014 CONTINUE
      WRITE(6,1016)
      NPRINT=1
1015 CONTINUE
1016 FORMAT(1H2,* ***** GREATER THAN 500 POINTS ON PLOT - TR
1UNCATED ******)
      IF(TIME.GE.T(IT))259,160
259 TIME=T(IT)
      LCYCL=0
      GO TO 73
160 ILINK=MAX0(0,ILINK-1)
      NPR=NPR+1
      DTP=DTP+DT

C
C   STORE VALUES FOR PRINTING
C
      IF(NPR.GE.NP.AND.DTP.GE.DTPMIN.AND.MEQ.EQ.0)62,65
62 CALL STORE
      IF (IFAIL) 63,63,535
63 CONTINUE
      IF(LT.GE.250) GOTO 130
65 CONTINUE

C
C   CHECK TIME LIMIT
C
73 CONTINUE
      CALLSPARE(TLFT)
      IF(TLFT.LE.2.000) GO TO 130

C
C   BRANCH TO EQUILIBRIUM ROUTINES
C
      IF((MEQ.EQ.1.OR.MEQ.EQ.3).AND.NEQ.GT.0)CALL EQUIL2
      IF(MEQ.GE.2)CALL EQUIL3
      IF(MEQ.NE.0)75,273

```

```

75 IF(IFAIL)174,174,575
575 WRITE(6,666)
    GO TO 130
174 LCYCL=0
273 IF((NPR.GE.NP.AND.DTP.GE.DTPMIN).OR.TIME.EQ.T(IT))274,175
274 CALL STORE
    IF (IFAIL) 275,275,535
275 CONTINUE
    IF(LT.GE.250) GOTO 130
    IF(TIME.EQ.T(IT))120,175

C
C   REDETERMINE TIME INCREMENTS
C
175 DFDCMA=0.
    DO 360 L=1,NC
        IF(JSK(L).GE.1)GO TO 360
        DFDC=0.
        DO 350 I=1,NR
            IF(ISK(I).GE.1)GO TO 350
            M1I=M1(I)
            M2I=M2(I)
            IF(M1I.EQ.L)DFDC=DFDC+FLOAT (KOEFF(L,I))*RK(I)*C(M2I)
            IF(M2I.EQ.L)DFDC=DFDC+FLOAT (KOEFF(L,I))*RK(I)*C(M1I)
350 CONTINUE
        DFDCAB=ABS (DFDC)
        IF(DFDCAB.GT.DFDCMA)DFDCMA=DFDCAB
360 CONTINUE
        DTREQ=ACCFAC/DFDCMA
        DTMX=DTMAX
        IF(MEQ.GT.0)DTMX=DTMXEQ
        IF(DT.GT.(1.4*DTREQ).AND.DT.GE.(2.*DTMIN).AND.(IT.NE.NT.OR.
1   IFR.EQ.0))365,370
365 DT=DT*0.5
    LCYCL=0
    GO TO 36
370 IF(DT.LT.(0.7*DTREQ).AND.DT.LE.(0.5*DTMX))375,36
375 DT=2.*DT
    ILINK=P-1

```



```

      GO TO 36
120 CONTINUE
C
C      DIFFERENTIAL EQUATIONS SOLVED
C
130 CONTINUE
C
C      BUFFER OUT LAST SET OF CONCENTRATIONS IF NEEDED
C
      IF (LTT.EQ.0) 135,132
132 BUFFER OUT (10,1) (CCL(1),CCL(1500))
      IF (UNIT (10)) 133,134,134
133 NBUFO=NBUFO+1
      GO TO 135
134 WRITE (6,670)
670 FORMAT (1X,*ERROR ON LAST BUFFER OUT,RUN TERMINATED*)
      GO TO 590
135 ENDFILE 10
C      DEFINE COLUMN HEADINGS
      DO 220 J=1,NC
220 AN(J)=7HMOLES/L
      DO 225 J=NC1,30
      AC(J)=5H
225 AN(J)=7H
      AC(NC1)=5HCOND
      AC(NC2)=5HABSC
      AC(NC3)=5HDT
      AN(NC1)=7H MHO/CM
      AN(NC2)=7H /CM
      AN(NC3)=7H SEC
C
C      ARRANGE RESULTS FOR OUTPUT.
C      ARRANGE COLUMN HEADINGS FOR OUTPUT
C
      IGROUP=(NC3+5)/6
      DO 150 IG=1,IGROUP
      IF (IPUNCH.GT.0) WRITE (7,315) NORUN,IG,LT,T(NT)
      DO 140 L=1,6

```

```

      IGL=(IG-1)*6+L
      AAC(L)=AC(IGL)
140  AAN(L)=AN(IGL)
      IF (IPUNCH) 142,142,141
141  WRITE (7,310) (AAC(L),L=1,6),(AAN(L),L=1,6)
142  CONTINUE
C
C      SET UP COUNTERS FOR BUFFER IN OPERATIONS
C
      LPT=0
      NBUFI=NBUFO
      REWIND 10
C
C      BUFFER IN ONE SET OF CONCENTRATIONS AND PRINT COLUMN HEADINGS
C
      DO 750 K=1,NBUFO
      WRITE (6,310) (AAC(L),L=1,6),(AAN(L),L=1,6)
      BUFFER IN (10,1) (CCL(1),CCL(1500))
      IF (UNIT (10)) 691,691,690
690  WRITE (6,669) NBUFO
669  FORMAT (1X,*ERROR ON LAST BUFFER IN, RUN TERMINATED*,6X,
      1*NO. OF BUFFER OPERATIONS*,I6)
      GO TO 590
691  IF (NBUFI-1) 692,692,694
692  IF (LTT.EQ.0) 694,693
693  LLT=LTT
      GO TO 695
694  LLT=50
      NBUFI=NBUFI-1
695  CONTINUE
C
C      LOOPS FOR REARRANGING DATA FOR OUTPUT
C
      DO 750 I=1,LLT
      DO 700 J=1,6
      IGL=(IG-1)*6+J
      700  CP(J)=CC(IGL,I)
C

```

```

C      PRINT AND PUNCH ONE LINE OF OUTPUT
C
      LPT=LPT+1
      IF (IPUNCH.GT.0) WRITE (7,313) TT(LPT),(CP(L),L=1,6)
      WRITE (6,313) TT(LPT),(CP(L),L=1,6)
750  CONTINUE
      IF (IPUNCH.GT.0) WRITE (7,998)
150  CONTINUE
C
C      REARRANGE THE OUTPUT DATA FOR PLOTTING. THE NUMBER OF PLOTS
C      IS GIVEN BY NPLOTS. THE NUMBER OF POINTS PER PLOT IS GIVEN BY
C      NPTS. THE MAXIMUM VALUES ARE NPLOTS = 5, NPTS = 500
C      CONDUCTANCE AND OPTICAL DENSITY ARE PLOTTED SEPERATELY
C
      IF (LPLOT.NE.0) 580,590
580  IF (NPTS.EQ.500) 585,581
581  J=1
      I=1
      DO 584 K=1,NPLOTS
      DO 584 L=1,NPTS
      CONCN(J,I)=CONCN(L,K)
      J=J+1
      IF (J.GE.501) 582,584
582  I=I+1
      J=1
584  CONTINUE
585  CALL PLOTIT (NPLOTS,NPTS,CONCN,ODCOND,POTIME)
590  IF (TLFT.LE.2.000)WRITE(6,667)
      IF (LT.GE.250)WRITE(6,668)
      IF (TLFT.LE.2.000) 600,1
C
C
C
200  FORMAT(1X,I4,I5)
201  FORMAT(3(5X,A5),3(1X,A1,3X,A5),5X,E15.2)
203  FORMAT(6X,I2,2X,A5,E10.3,3E15.3,E10.3)
205  FORMAT(5X,E15.3,E10.3,2A5,2E10.3,5I3,4X,I1)
206  FORMAT(E10.3,I5,4E10.3,I5)

```

```

300 FORMAT(1X,10HRUN NUMBER,I5,56X,A10//)
301 FORMAT(6X,A5,5H + ,A5,5H = ,A5,3(1X,A4,A5),2X,2HK(,
1 12,3H) =,1PE10.2)
302 FORMAT(//6X,2HNO,2X,6HCHARGE,3X,4HNAME,5X,1HG, 9X,1HS,11X,2HCI,
1 10X,4HEQCO,7X,3HEXT/)
303 FORMAT (I8,4X,I2,5X,A5,F7.3,2(3X,1PE9.3,1X),F10.3,2X,1PE10.3)
304 FORMAT (1H1,5(/),5X,2HNO,4X,4HTIME,4X,9HDOSE RATE,3X,7HSPECIES,
16X,4HCSK1,7X,4HCSK2,7X,9HREACTIONS,3X,1HI/79X,1HE/12X,3HSEC,5X,
28HEV/L-SEC,4X,7HSKIPPED,5X,7HMOLES/L,4X,7HMOLES/L,6X,7HSKIPPED,
34X,1HQ/)
305 FORMAT (I8,2(2X,1PE8.2),2X,A5,1X,A5,2(2X,1PE9.3),5I3,1X,I1)
306 FORMAT (1H0,/6X,15HACCURACY FACTOR,1PE10.2/
1 6X,24HVALUES PRINTED OUT EVERY,I6,7H CYCLES/
26X,23HMINIMUM PRINT INTERVAL ,1PE10.3,4HSEC /
3 6X,23HMINIMUM TIME INCREMENT ,1PE10.3,4H SEC/
4 6X,23HMAXIMUM TIME INCREMENT ,1PE10.3,4H SEC/
5 6X,22HSAME IF EQUILIBRIUM IS,/6X,8HCOMPUTED,15X,1PE10.3,4H SEC)
307 FORMAT(6X,*TIME INCREMENTS FROZEN IN LAST TIME INTERVAL*)
308 FORMAT(///)
310 FORMAT (1H1,5(/),5X,4HTIME,3X,6(5X,A5,1X)//
15X,7HSECONDS,6(4X,A7)//)
313 FORMAT (2X,7(1PE11.3))
315 FORMAT (I4,1H*,I1,1H*,I3,1PE10.3/)
400 FORMAT (//6X,*INITIAL CONDUCTIVITY =*,1PE11.3,1X,*MHO/CM*/
1 6X,*INITIAL ABSORBANCE =*,1PE11.3,1X,*CM*//)
666 FORMAT(1X,*RUN ABANDONED*)
667 FORMAT(1X,*LESS THAN 2 SEC LEFT, SEQUENCE TERMINATED*)
668 FORMAT(1X,*PRINT LIMIT REACHED, RUN TERMINATED*)
998 FORMAT(79X,1H-)
999 FORMAT(1H1)
600 STOP
END

```

SUBROUTINE SCAN(CHARGE,CHEM)

INTEGER CHEM,CHARGE,C(4)

C

DO 30 N=1,4

ENCODE(7,10,M)N

10

FORMAT(1H(,11,5HX,A1))

DECODE(5,M,CHEM)C(N)

IF(C(N).EQ.1H-)CHARGE=CHARGE-1

IF(C(N).EQ.1H+)CHARGE=CHARGE+1

30

CONTINUE

RETURN

END

SUBROUTINE STORE

C

C

C

C

C

CALCULATE CONDUCTIVITY AND ABSORBANCE, STORE SET OF OUTPUT VALUES
THIS VERSION OF STORE BUFFERS OUT THE OUTPUT VALUES IN BLOCKS OF
30 * 50 VALUES

INTEGER CHARGE

C

DIMENSION CCL(1500)

C

EQUIVALENCE (CC(1,1),CCL(1))

C

COMMON CC(30,50),CONCN(500,5),KOEFF(27,30),KOEFL(27,30),

1 ODCOND(500)

C

COMMON/BLOCK1/ AC(30),C(30),CHARGE(28),NC

C

COMMON /BLOCK2/ IFAIL

C

COMMON /BLOCK6/ ABSI,CONDI,DTP,EQCO(28),EXT(28),LT,

```

C      1NC1,NC2,NC3,NPR,TIME,TT(250),LTT
C
C      COMMON /BLOCK7/ DT
C
C      COMMON /BLOCK10/ MPLOT,NBUFO,PTT(30),XC(10)
C
C      CONDC=-CONDI
C      ABSC=0.
C
C      ABSC=0.0 RESULTS IN OPTICAL DENSITY VALUES WHICH ARE REFERENCED
C      TO AN ARBITRARY ZERO OF OPTICAL DENSITY AT TIME EQUALS ZERO
C
      LT=LT+1
      LTT=LTT+1
      DO 20 L=1,NC
      CC(L,LTT)=C(L)
      TT(LT)=TIME
      CONDC=CONDC+C(L)*EQCO(L)*ABS(FLOAT(CHARGE(L)))*0.001
20  ABSC=ABSC+C(L)*EXT(L)
      CC(NC1,LTT)=CONDC
      CC(NC2,LTT)=ABSC
      CC(NC3,LTT)=DT
      IF (NC3-30) 25,40,40
25  NC4=NC3+1
      DO 30 L=NC4,30
30  CC(L,LTT)=0.0
      NPR=0
40  DTP=0.0
      IF (LTT.EQ.50) 50,55
50  BUFFER OUT (10,1) (CCL(1),CCL(1500))
      IF (UNIT(10)) 60,61,61
60  LTT=0
      NBUFO=NBUFO+1
      GO TO 55
61  WRITE (6,70) NBUFO
      IFAIL=1
70  FORMAT (1X,*ERROR ON LAST BUFFER OUT, RUN TERMINATED*,6X,
      1*NUMBER OF BUFFER OPERATIONS*,I6)

```

55 CONTINUE
RETURN
END

```
      SUBROUTINE EQUIL1
C
C      READ AND PRINT EQUILIBRIUM EQUATIONS
C
C      INTEGER AC,AE,BLANK,CHARGE
C
C      COMMON/BLOCK1/ AC(30),C(30),CHARGE(28),NC
C
C      COMMON /BLOCK2/ IFAIL
C
C      COMMON /BLOCK3/ NEQ
C
C      COMMON /BLOCK4/ AE(3,11),EQ(11),EQ2(11),LEQ(4,11)
C
C      DIMENSION ISHIFT(10),ISKIP(10)
C
C      DATA (BLANK=5H      )
C      DO 510 K=1,10
C      KK=K
C      READ(5,211)(AE(M,K),M=1,3),EQ(K)
C      IF(AE(1,K)-BLANK)510,511,510
C      510 WRITE(6,311)(AE(M,K),M=1,3),EQ(K)
C      511 NEQ=KK-1
C      IF(NEQ)530,530,519
C      519 CONTINUE
C      IDENTIFY SPECIES IN EQUILIBRIUM
C      DO 520 K=1,NEQ
C      DO 520 M=1,3
C      DO 515 L=1,NC
C      LL=L
C      IF(AC(L)-AE(M,K))515,512,515
```

```

512 LEQ(M,K)=L
    GO TO 520
515 CONTINUE
    IF(LL-NC)520,520,526
520 CONTINUE
C   ERROR CHECK
    DO 525 K=1,NEQ
    IF(AE(1,K)-AE(1,1))526,525,526
525 CONTINUE
C   CHECK FOR 2ND DISSOCIATION STAGE. RENUMBER
    ISKIP(1)=0
    ISHIFT(1)=0
    DO 630 K=1,NEQ
    ISKIP(K+1)=0
    ISHIFT(K+1)=ISHIFT(K)
    LEQ(4,K)=NC+1
    EQ2(K)=0.
    IF(ISKIP(K))630,605,630
605 IF(LEQ(2,K)-LEQ(3,K+1))630,610,630
610 IF(LEQ(3,K)-LEQ(2,K+1))615,526,615
615 EQ2(K)=EQ(K+1)
    LEQ(4,K)=LEQ(2,K+1)
    ISHIFT(K+1)=ISHIFT(K)+1
    ISKIP(K+1)=1
630 CONTINUE
    DO 650 K=1,NEQ
    IF(ISKIP(K))650,635,650
635 K11111=K-ISHIFT(K)
    EQ(K11111)=EQ(K)
    EQ2(K11111)=EQ2(K)
    DO 640 M=1,4
640 LEQ(M,K11111)=LEQ(M,K)
650 CONTINUE
    NEQ=NEQ-ISHIFT(NEQ)
    GO TO 530
526 WRITE(6,777)
    IFAIL=1
530 RETURN

```



```

211 FORMAT(3(5X,A5),5X,E10.3)
311 FORMAT(6X,A5,5H *    ,A5,5H =    ,A5,4H *    ,E10.3)
777 FORMAT(1X,*ERROR IN EQUILIBRIUM EQUATIONS*)
END

```

```

SUBROUTINE EQUIL2
C
C   COMPUTE EQUILIBRIUM OF IONIC SPECIES
C
C   INTEGER AC,AE,CHARGE
C
C   COMMON/BLOCK1/ AC(30),C(30),CHARGE(28),NC
C
C   COMMON /BLOCK2/ IFAIL
C
C   COMMON /BLOCK3/ NEQ
C
C   COMMON /BLOCK4/ AE(3,11),EQ(11),EQ2(11),LEQ(4,11)
C
C   COMMON /BLOCK5/ DELTA
C
C   DIMENSION HPLUS(3),TOTAL(10)
C
C   LEQ1=LEQ(1,1)
C   CH=FLOAT(CHARGE(LEQ1))
C   HPLUS(1)=C(LEQ1)
C   DO 540 K=1,NEQ
C   LEQ2K=LEQ(2,K)
C   LEQ3K=LEQ(3,K)
C   LEQ4K=LEQ(4,K)
540 TOTAL(K)=C(LEQ2K)+C(LEQ3K)+C(LEQ4K)
C   DO 560 NSTEP=1,20
C   DO 555 I=2,3
C   DO 545 K=1,NEQ
C   LEQ2K=LEQ(2,K)

```

```

      LEQ3K=LEQ(3,K)
      LEQ4K=LEQ(4,K)
      C(LEQ3K)=TOTAL(K)/(1.+EQ(K)/HPLUS(I-1)+EQ(K)*EQ2(K)/HPLUS(I-1)**2)
      C(LEQ2K)=(EQ(K)*C(LEQ3K))/HPLUS(I-1)
545  C(LEQ4K)=(EQ2(K)*C(LEQ2K))/HPLUS(I-1)
      HPLUS(I)=HPLUS(I-1)
      DO 551 L=1,NC
      IF(CHARGE(L))550,551,550
550  HPLUS(I)=HPLUS(I)-CH*FLOAT (CHARGE(L))*C(L)
551  CONTINUE
      CHECK=ABS ((HPLUS(I)-HPLUS(1))/(HPLUS(I)+HPLUS(1)))
      IF(CHECK-DELTA*0.1)553,553,555
553  C(LEQ1)=(HPLUS(I)+HPLUS(I-1))/2.
      GO TO 562
555  C(LEQ1)=HPLUS(I)
      HPLUS0=HPLUS(1)
      HPLUS(2)=(HPLUS(2)**2-HPLUS(1)*HPLUS(3))/(2.*HPLUS(2)-HPLUS(1)
1      -HPLUS(3))
      C(LEQ1)=HPLUS(1)
      CHECK=ABS ((HPLUS(1)-HPLUS0)/(HPLUS(1)+HPLUS0))
      IF(CHECK-DELTA)562,562,560
560  CONTINUE
      IFAIL=1
      WRITE(6,777)
      GO TO 570
562  DO 565 K=1,NEQ
      LEQ2K=LEQ(2,K)
      LEQ3K=LEQ(3,K)
      LEQ4K=LEQ(4,K)
      C(LEQ3K)=TOTAL(K)/(1.+EQ(K)/HPLUS(1)+EQ(K)*EQ2(K)/HPLUS(1)**2)
      C(LEQ2K)=EQ(K)*C(LEQ3K)/HPLUS(1)
565  C(LEQ4K)=EQ2(K)*C(LEQ2K)/HPLUS(1)
777  FORMAT(1X,*DIVERGENCE IN EQUIL2*)
570  RETURN
      END

```

SUBROUTINE EQUIL3

```

C      COMMON CC(30,50),CONCN(500,5),KOEFF(27,30),KOEFL(27,30),
1      ODCOND(500)
C
C      COMMON /BLOCK1/ NN(30),C(30),NNN(28),NC
C
C      COMMON /BLOCK2/  IFAIL
C
C      COMMON /BLOCK5/ DELTA
C
C      COMMON /BLOCK8/ ISK(30),ISK3(30),JSK(30),JSK3(30),
1      M1(30),M2(30),NR,RF(27),RK(31)
C
      DO 150 N=1,20
      TEST=0.
      DO 100 J=1,NC
      IF(JSK3(J).NE.0)5,100
5  CO=C(J)
      AO=RF(J)
      A1=0.
      A2=0.
      DO 50 I=1,NR
      IF(ISK(I).NE.0.AND.ISK3(I).EQ.0)50,7
7  CONTINUE
      M1I=M1(I)
      M2I=M2(I)
      IF(KOEFL(J,I).EQ.-2)A2=A2+RK(I)*FLOAT (KOEFF(J,I))
      IF(KOEFL(J,I).EQ.-1)10,30
10 IF(M1I.EQ.J)15,20
15 A1=A1+RK(I)*FLOAT (KOEFF(J,I))*C(M2I)
20 IF(M2I.EQ.J)25,30
25 A1=A1+RK(I)*FLOAT (KOEFF(J,I))*C(M1I)
30 IF(KOEFL(J,I).EQ.0.AND.KOEFF(J,I).NE.0)AO=AO+RK(I)*FLOAT (KOEFF
1  (J,I))*C(M1I)*C(M2I)
50 CONTINUE
      IF(A2.EQ.0.)C(J)=-AO/A1
      IF(A2.NE.0.)C(J)=(-A1-SQRT (A1*A1-4.*AO*A2))/(2.*A2)

```

```

      TEST=TEST+ABS (C(J)-C0)
100  CONTINUE
      IF (TEST.LE.2.*DELTA)GO TO 160
150  CONTINUE
      IFAIL=1
      WRITE(6,666)
160  RETURN
666  FORMAT(1X,*DIVERGENCE IN EQUIL3*)
      END

```

```

      SUBROUTINE READEQ
C
      REAL K(2),K12,K21,K23,K32
C
      COMMON/BLOCK1/ AC(30),C(30),CHARGE(28),NC
C
      COMMON /BLOCK11/  CI(30),MEQA
C
      COMMON /BLOCK15/ K12,K21,K23,K32
C
      DIMENSION EK(2),AEQ(3),SP(2),CONC(2)
C
      DO 1 I=1,2
      READ(5,2)AEQ(I),SP(I),AEQ(I+1),EK(I),K(I)
2      FORMAT(5X,A5,5X,A5,5X,A5,30X,2E10.2)
      IF(AEQ(I).EQ.5H      )GO TO 3
1      CONTINUE
      DO 4 I=1,2
      DO 4 N=1,NC
      IF (SP(I).EQ.AC(N))CONC(I)=CI(N)
4      CONTINUE
      K12=CONC(1)*K(1)
      K21=K12/EK(1)
      K23=CONC(2)*K(2)
      K32=K23/EK(2)

```

```

      DO 5 N=1,NC
5      IF(AEQ(1).EQ.AC(N))MEQA=N
      WRITE(6,309)
309    FORMAT(1H1,*    EQUILIBRIUM EQUATIONS*,///)
      WRITE(6,320)AEQ(1),SP(1),AEQ(2),K12,K21,EK(1)
      WRITE(6,320)AEQ(2),SP(2),AEQ(3),K23,K32,EK(2)
320    FORMAT(10X,A5,*  +  *,A5,*  =  *,A5,20X,*KF=*,E10.3,*  KB=*,E10.3,
$      *    EQ CONST=*,E10.3,/)
3      CONTINUE
      RETURN
      END

```

```

      SUBROUTINE EQUIL4
C
      INTEGER CALL
      REAL L2,L3
C
      COMMON/BLOCK1/ AC(30),C(30),CHARGE(28),NC
C
      COMMON /BLOCK7/ DT
C
      COMMON /BLOCK12/ CALL,L
C
      COMMON /BLOCK14/ A10,A20,A30,L2,L3,T1,T2,T3,U1,U2,U3,V1,V2,V3
C
      CALL=CALL+1
      IF(CALL.NE.1)GO TO 1
      A10=C(L)
      A20=C(L+1)
      A30=C(L+2)
      CALL COMP
      EX1=EXP(-DT*L2)
      EX2=EXP(-DT*L3)
      C(L)=T1+T2*EX1+T3*EX2

```

```

1  GO TO 3
   CONTINUE
   IF(CALL.NE.2)GO TO 2
   C(L)=U1+U2*EX1+U3*EX2
   GO TO 3
2  CONTINUE
   C(L)=V1+V2*EX1+V3*EX2
3  CONTINUE
   IF(CALL.EQ.3)CALL=0
   RETURN
   END

```

SUBROUTINE COMP

```

C  REAL L2,L3,K12,K21,K23,K32
C
C  COMMON /BLOCK14/ A10,A20,A30,L2,L3,T1,T2,T3,U1,U2,U3,V1,V2,V3
C
C  COMMON /BLOCK15/ K12,K21,K23,K32
C
C
P=K12+K21+K23+K32
Q2=(P*P)-4.0*(K12*K23+K21*K32+K12*K32)
Q=SQRT(Q2)
L2=0.5*(P+Q)
L3=0.5*(P-Q)
X=K12/K21
Y=(K12-L2)/K21
Z=(K12-L3)/K21
A=K23/K32
B=K23/(K32-L2)
C=K23/(K32-L3)
D=Z*(C-A)-Y*(B-A)*(Z-X)/(Y-X)
Q3=A10*X*Y*(B-A)/(D*(Y-X))-A20/D*(A+Y*(B-A)/(Y-X))+A30/D
Q2=(A20-X*A10-(Z-X)*Q3)/(Y-X)

```

A50.

```
Q1=A10-Q2-Q3
T1=Q1
T2=Q2
T3=Q3
U1=Q1*X
U2=Q2*Y
U3=Q3*Z
V1=Q1*X*A
V2=Q2*Y*B
V3=Q3*Z*C
RETURN
END
```

```
SUBROUTINE PLOTST(NPLOTS,NPTS)
```

```

C
COMMON  CC(30,50),CONC(500,5),KOEFF(27,30),KOEFL(27,30),
1      ODCOND(500)
C
COMMON/BLOCK1/ AC(30),C(30),CHARGE(28),NC
C
COMMON /BLOCK6/ ABSI,CONDI,DTP,EQCO(28),EXT(28),LT,
1INC1,NC2,NC3,NPR,TIME,TT(250),LTT
C
COMMON /BLOCK9/ DTPLOT,I,NRI(2),NPRINT,PLTIME(500)
C
COMMON /BLOCK10/ MPLOT,NBUFO,PTT(30),XC(10)
C
COMMON /BLOCK11/ CI(30),MEQA
C
INTEGER CHARGE
```

```

3   PLTIME(1)=0.
    DO 7 K=1,NC
7   C(K)=CI(K)
6   CONTINUE
    J=0
    DO 1 N=1,NC
      IF(PTT(N).EQ.0.)GO TO 4
      IF(J.GE.4)GO TO 2
      J=J+1
      CONC(I,J)=C(N)
      IF (CONC(I,J).GT.XC(J)) XC(J)=CONC(I,J)
    GO TO 4
2   CONTINUE
    IF(NPRINT.EQ.0)WRITE(6,10)
    NPRINT=1
4   CONTINUE
1   CONTINUE
    IF (PTT(28).EQ.0.0) GO TO 21
    ODCOND(I)=-CONDI
    DO 20 N=1,NC
20  ODCOND(I)=ODCOND(I) + C(N)*EQCO(N)*ABS(FLOAT(CHARGE(N)))*0.001
21  CONTINUE
    IF (PTT(29).EQ.0.0) GO TO 31
    ODCOND(I)=0.0
    DO 30 N=1,NC
30  ODCOND(I)=ODCOND(I) + C(N)*EXT(N)
31  CONTINUE
    IF(NRI(1).EQ.0.OR.NRI(2).EQ.0)GO TO 5
    J=J+1
    N1=NRI(1)
    N2=NRI(2)
    CONC(I,J)=C(N1)/C(N2)
    IF (CONC(I,J).GT.XC(J)) XC(J)=CONC(I,J)
5   CONTINUE
    NPTS=I
    NPLOTS=J
    DTPLOT=0.
10  FORMAT(1H2,*  ++++++ GREATER THAN 5 GRAPHS - TRUNCATED ++

```


1++++++*)

RETURN
END

SUBROUTINE PLOTIT (NPLOTS,NPTS,CONCN,ODCOND,POTIME)

C

COMMON /BLOCK10/ MPLOT,NBUFO,PTT(30),XC(10)

C

DIMENSION CONCN(NPTS,NPLOTS),ODCOND(NPTS),POTIME(NPTS)

C

DIMENSION M(10)

C

C

IF (NPLOTS.EQ.0) 11,10

10 DO 1 I=1,NPLOTS

M(I)=ALOG10(XC(I))-1.0

AB=10.**M(I)

DO 1 J=1,NPTS

CONCN(J,I)=CONCN(J,I)/AB

1

CONTINUE

11 CONTINUE

IF (MPLOT.NE.0) GO TO 2

CALL PLOTS (5HSCGSL,5)

CALL XLIMIT(210.)

MPLOT=1

2

CONTINUE

IF (NPLOTS.EQ.0) 21,20

20 CONTINUE

CALL AUTPLT(POTIME,CONCN,NPTS,NPLOTS,6H*TIME*,6H*CONC*)

21 CONTINUE

IF (PTT(28).EQ.1.0) CALL AUTPLT (POTIME,ODCOND,NPTS,1,6H*TIME*,
113H*CONDUCTANCE*)

IF (PTT(29).EQ.1.0) CALL AUTPLT (POTIME,ODCOND,NPTS,1,6H*TIME*,
117H*OPTICAL DENSITY*)

RETURN

END

C

SUBROUTINE SPARE(TLFT)

CALL SECOND (T)

ALIM=40.0

TLFT=ALIM - T

RETURN

END

RUN NUMBER

8

710630

OH + CL- = CL +
 CL + CL- = CL2- +
 CL2- + DUMMY = CL + CL-

K(1) = 4.00E+07
 K(2) = 2.00E+10
 K(3) = 6.67E+05

NO	CHARGE	NAME	G	S	CI	EQCO	EXT
1	-0	CL	0.000	0.	0.	0.000	-0.
2	-1	CL2-	0.000	0.	*	-0.000	-0.
3	-0	OH	2.600	0.	2.000E-06	-0.000	-0.
4	-1	CL-	0.000	*	2.000E-03	-0.000	-0.
5	-1	OH-	-0.000	*	2.500E-10	-0.000	-0.
6	-0	DUMMY	0.000	*	1.000E+00	-0.000	-0.

INITIAL CONDUCTIVITY = 0. MHO/CM
 INITIAL ABSORBANCE = 0. /CM

NO	TIME	DOSE RATE	SPECIES	CSK1	CSK2	REACTIONS	I
	SEC	EV/L-SEC	SKIPPED	MOLES/L	MOLES/L	SKIPPED	E
1	2.00E-10	0.	DUMMY OH-	1.000E+00	2.500E-10	-0 -0 -0 -0 -0	*
2	1.00E-06	0.	CL-	2.000E-03	*	-0 -0 -0 -0 -0	*
3	3.00E-06	0.		*	*	-0 -0 -0 -0 -0	*

TIME	CL	CL2-	OH	CL-	OH-	DUMMY
SECONDS	MOLES/L	MOLES/L	MOLES/L	MOLES/L	MOLES/L	MOLES/L
0.	0.	-0.	2.000E-06	2.000E-03	2.500E-10	1.000E+00
2.000E-10	3.190E-11	9.600E-14	2.000E-06	2.000E-03	2.500E-10	1.000E+00
1.420E-08	1.734E-09	5.367E-10	1.998E-06	2.000E-03	2.500E-10	1.000E+00
1.262E-07	4.145E-09	1.595E-08	1.980E-06	2.000E-03	2.500E-10	1.000E+00
3.182E-07	4.605E-09	4.566E-08	1.950E-06	2.000E-03	2.500E-10	1.000E+00
5.102E-07	5.034E-09	7.495E-08	1.920E-06	2.000E-03	2.500E-10	1.000E+00
7.022E-07	5.458E-09	1.038E-07	1.891E-06	2.000E-03	2.500E-10	1.000E+00
8.942E-07	5.874E-09	1.322E-07	1.862E-06	2.000E-03	2.500E-10	1.000E+00
1.000E-06	6.101E-09	1.477E-07	1.846E-06	2.000E-03	2.500E-10	1.000E+00
1.160E-06	6.441E-09	1.708E-07	1.823E-06	2.000E-03	2.500E-10	1.000E+00
1.352E-06	6.843E-09	1.982E-07	1.795E-06	2.000E-03	2.500E-10	1.000E+00
1.544E-06	7.239E-09	2.252E-07	1.768E-06	2.000E-03	2.500E-10	1.000E+00
1.736E-06	7.628E-09	2.517E-07	1.741E-06	2.000E-03	2.500E-10	1.000E+00
1.928E-06	8.012E-09	2.779E-07	1.714E-06	2.000E-03	2.500E-10	1.000E+00
2.120E-06	8.390E-09	3.036E-07	1.688E-06	2.000E-03	2.500E-10	1.000E+00
2.312E-06	8.762E-09	3.290E-07	1.662E-06	2.000E-03	2.500E-10	1.000E+00
2.504E-06	9.128E-09	3.539E-07	1.637E-06	2.000E-03	2.500E-10	1.000E+00
2.696E-06	9.489E-09	3.785E-07	1.612E-06	2.000E-03	2.500E-10	1.000E+00
2.888E-06	9.845E-09	4.027E-07	1.587E-06	2.000E-03	2.500E-10	1.000E+00
3.000E-06	1.005E-08	4.167E-07	1.573E-06	2.000E-03	2.500E-10	1.000E+00

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