MECHANISMS OF EXCHANGE REACTIONS IN SOLIDS

by

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To

my dear parents

Basilio and Mercedes Passaglia

and my dear sister and brothers

Preface

This dissertation describes the result of my work as a research student, at the Chemical Laboratory of the University of Cambridge, during the period October 1976 - October 1980, and includes nothing which is the outcome of work done in collaboration. No part of the dissertation has been, or is being, submitted for any degree or diploma or other qualification at any other university. This dissertation is less than 60,000 words in length, and is the result of my own work unless due reference is given.

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Summary

The solid-state exchange reaction between two normal lattice species has been investigated in the compounds $[Fe\ (H_2O)_6][Fe\ EDTA\ (H_2O)]_3.H_2O$, $[Co\ (NH_3)_5\ Cl]Cl_2$ and in the chromium (III) oxalates $[Cr\ (H_2O)_6][Cr\ (C_2O_4)_3]$ and $[Cr\ (C_2O_4)(H_2O)_4][Cr\ (C_2O_4)_2(H_2O)_2]$ where the exchanging species occupy two different lattice sites and have the same oxidation state. In these systems the exchanging species are either ions on ordinary lattice sites and complex metal ions as in the compounds $[Fe\ (H_2O)_6][Fe\ EDTA\ (H_2O)]_3$ H_2O and $Cr_2(C_2O_4)_3.6H_2O$, or ligands and outer anions as in the compound $[Co\ (NH_3)_5Cl]Cl_2$.

The exchange between the iron atoms in the compound $[Fe\ (H_2O)_6][Fe\ EDTA\ (H_2O)]_3.H_2O$ starts at 100°C, increases sharply in a narrow interval of temperature just below the temperature of decomposition and is correlated with the thermal decomposition process at temperatures higher than 140°C. Measurements on a dehydrated sample showed lower values for exchange than in the hydrated sample. The effects of γ-irradiation and crushing the crystals before heating were investigated: the two treatments did not induce exchange, but crushing enhanced the subsequent thermal exchange while γ-irradiation had no effect.

Exchange proceeds very slowly in the compound $[Co\ (NH_3)_5Cl]Cl_2$ even at temperatures as high as 170°C, when decomposition begins. Crushing and γ-irradiation failed to induce exchange or to enhance thermal exchange, but different preparations of the labelled compound gave different results. Exchange isothermals of the compound labelled in the cationic and in the anionic sides overlapped, giving evidence that a true exchange reaction was involved.

Exchange in the chromium (III) oxalates was found to be related to the decomposition process involving transfer of ligands.

The kinetics of the exchange in all systems was interpreted in terms of a model which assumed a set of first-order processes with a spectrum of energies of activation.

The mechanisms of these processes are discussed.

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CHAPTER 1 - GENERAL INTRODUCTION

1.1 Introduction

The most recent investigations of exchange reactions in the solid state have been exploring the situation where the exchanging species are normal lattice entities. Solid-state exchange reactions between normal lattice occupants are also the subject of this investigation, whose aim is to achieve a better understanding of the mechanisms of the exchange processes in the solid state.

Most of the earliest studies of exchange reactions in the solid state were mainly directed towards elucidating the structure of compounds. Solid compounds containing atoms of the same element which may or may not be in different chemical states can be investigated using radioactive tracers, useful in determining whether these atoms pass through a state of chemical equivalence during the formation or decomposition of the solid.

As early as 1924, Zintl and Rauch synthesised $Pb_2O_3.3H_2O$ using radioactive Pb (II) and inactive Pb (IV). This solid was then decomposed and the two types of lead were separated without changing the original distribution of radioactivity, proving that the divalent and tetravalent lead atoms were at no time equivalent (Zintl & Rauch 1924).

In order to find out whether $H_4Cr_3O_8.xH_2O$ is better formulated as $H_4Cr_3(IV)O_8.xH_2O$ or $H_4Cr_2(III)Cr(VI)O_8.xH_2O$, Aten and collaborators (1953) prepared the substance by mixing an aqueous solution containing radioactive Cr(III) with one containing inactive $Cr(VI)O_4^{2-}$ ions. The solid product was then dissolved and CrO_4^{2-} was precipitated as $PbCrO_4$ and counted.

Less than 1% of the original activity was found in the precipitated fraction, indicating clearly that the chromium atoms were not equivalent at any stage of the synthesis-decomposition process.

The equivalence of atoms in the structure of other compounds of this kind was also investigated using radioactive tracers to check the exchange during the formation and decomposition of the solid. It is now known that compounds like the thallium halides, Tl_2X_3, are better written as $Tl(I)_3[Tl(III)Cl_6]$ (Lorthioir & Michel 1964, Whitney et al. 1948).

It has also been shown that the introduction of radioactive Sb(III) into hexachloroantimoniates does not yield equal amounts of radioactive Sb(III) and Sb(V) on decomposition, as would be expected if all the antimony ions in the crystal were equivalent (Turco & Mazzon 1953, Turco & Sordillo 1955a).

This type of investigation has also been carried out on nickel cyanide. The observation that solid nickel cyanide contains two non-equivalent kinds of nickel (Long 1951) indicates that the empirical formula, $Ni(CN)_2$, is better written as $Ni[\bar{N}i(CN)_4]$. In this compound both atoms are in the same oxidation state.

The study of exchange reactions in the solid system received an impetus with the suggestion that annealing reactions following nuclear changes could be interpreted as exchange reactions (Harbottle & Sutin 1959). During the 60's, exchange reactions in the solid state were widely studied in systems made in an attempt to simulate neutron-irradiated solids. The exchanging radioactive entity was introduced into the lattice of these "doped" systems by means of several different techniques. Numerous doped systems of this kind have been explored and it has become clear that the reactions occurring between the dopant and the normal lattice species are actually exchange reactions. An account of these studies is given in sections 1.4-1 and 1.4-2.

With the exception of Schmidt's experiment in 1965, it was not until 1975 that exchange between normal lattice entities was explored. These experiments concentrated on solid compounds containing a given element in two sites of different coordination, or in different states of oxidation, or both. The possibility of inducing exchange thermally or by other means was investigated to discover whether exchange between normal lattice species could take place in the solid state, and to obtain information about the mechanisms of such reactions.

The important difference between experiments on these systems and on the doped systems is that, in the latter, the dopant is always at a concentration which is several orders of magnitude less than its exchanging partner, so that the exchange can only be followed in one direction. Further, the crystal location and even the exact identity of the dopant are not necessarily known exactly. When normal lattice entities are involved all these difficulties disappear.

The available experimental results of studies on exchange reactions in the solid state between normal lattice species are presented in section 1.4-4.

Solid-state isotopic exchange reactions that take place either in doped systems or between normal lattice entities show a resemblance to the annealing reactions following nuclear transformations in solids. Because of this connection between the two phenomena the next two sections, 1.2 and 1.3, will be devoted to the chemical effects of nuclear transformations in solids and to the post-recoil annealing effects, respectively.

1.2 The chemical effects of nuclear transformations

The first experiment in which attention was focussed on the chemical changes following recoil after a nuclear transformation was carried out in 1934 by Szilard and Chalmers, who extracted radioactive iodine from a sample of ethyl iodide that had been bombarded with thermal neutrons. The nuclear event was accompanied by a chemical event: the iodine-carbon bond was broken when a ^{127}I nucleus was transformed by neutron capture to ^{128}I (Szilard & Chalmers 1934). These authors (later) suggested (1934) that the observed bond-breaking was due to the transfer of momentum from the captured neutron to the compound nucleus, an observation now known to be incorrect since in a thermal-neutron capture the incident neutron cannot impart enough energy to the nucleus to cause rupture of the bond. Fermi and co-workers (Amaldi et al. 1935) provided a more ingenious explanation: upon capture of thermal neutron, gamma rays were emitted from the excited compound nucleus and the momentum necessary to break the bond was supplied by the recoil from these rays.

Let us suppose that the excitation energy of the compound nucleus is carried away by a single gamma ray of energy E_γ, having a momentum $P_\gamma = E_\gamma/c$. By conservation of momentum, the recoil energy is $E_r = P_\gamma^2/2M = E_\gamma^2/2Mc^2$, where M is the mass of the atom. A more convenient expression for the recoil energy is

$$E_r = \frac{537E_\gamma^2}{M} \text{ eV}$$

where E_γ is in units of MeV and M in amu.

Since the C-I bond energy is 2.0 eV we can see that the emission of a gamma photon of only 1 MeV energy would be enough to lead to bond rupture and produce a recoil iodine atom (M = 127) having an energy of 4.2 eV (Harbottle 1965).

This process has been used in the preparation of radioisotopes of high specific activity for medical and industrial purposes.

D'Agostino (1935), working with potassium permanganate irradiated with neutrons, found that only 80% of the ^{56}Mn could be separated from the permanganate. The fact that 20% of the events reformed the original type of complex ion was very disconcerting since the great majority of Mn-O bonds should have been broken by the mechanical recoil imparted to the nucleus by the emitted gamma rays. Since then, several experiments have demonstrated that a considerable part of the total activity can remain in the target molecule (e.g. Harbottle & Maddock 1979).

The radioactive fraction found in the parent form has come to be called the "retention" and it is mainly the result of a reaction of the recoil atom with its surroundings after the nuclear event.

Various theories have been proposed to explain the recombination of the recoil atom with the parent molecule (e.g. Harbottle & Sutin 1959).

The retention can be divided into four parts (Vargas &

Maddock 1979): $R_o = R_i + R_{ii} + R_{iii} + R_{iv}$. The first part, R_i, is due to failure of the bond to rupture; the second, R_{ii}, can be attributed to a very rapid reformation of the molecule with some or all of the same constituent atoms; R_{iii} is due to reformation reactions involving the high-energy recoil atoms (the so-called "hot" atoms - this component is a result of genuine hot-atom reactions); and R_{iv} arises from reformation reactions involving thermalised-product species.

It is very difficult to study the behaviour of the recoil particle as it loses its energy (a hot reaction takes place in a few picoseconds). Nevertheless, it is possible to obtain more information about the processes occurring in the irradiated solid by studying the reactions involving the thermalised species. Once the recoiling atom has been thermalised the subsequent reactions are described as annealing reactions.

1.3 Annealing reactions

Reactions involving the thermalised species formed in a solid compound more than 1 nanosecond after the nuclear change are known as annealing reactions. They take place between the radioactive product, the fragments and the unchanged lattice species in the terminal zone. They are called annealing reactions because they tend to reform the parent matrix species. These reactions are studied to understand the mechanisms by which they take place and also to discover the nature and environment of the species formed after the nuclear change.

Annealing reactions can be induced by treating the solid in different ways after irradiation; thus heating, exposure to radiation, and other treatments result in an increase of the retention.

Williams (1948) was the first to record an example of annealing, in this case induced by ionizing radiation. He reported that the specific activity of radioactive antimony produced by irradiation of antimony pentafluoride and ammonium fluometa antimonate (NH_4SbF_6) decreased with increasing time of irradiation; there was a radiation-induced back-reaction which returned the separable $^{124}Sb(III)$ to a form indistinguishable from the parent.

Soon after this, Green and Maddock (1949) found that the retention of ^{51}Cr in neutron-irradiated solid potassium chromate crystals could be increased simply by heating. Similar annealing effects were subsequently found in potassium permanganate (Aten & Van Berkum 1950) and in potassium bromate (Cobble & Boyd 1952). It is now known that nearly all irradiated systems show an increase in retention on heating.

Annealing processes have also been reported which have been induced in several other ways, such as by irradiation by light (Herr 1952), by compression (Andersen & Maddock 1963, Andersen 1963) and by ultrasonic and shock excitation (Getoff 1965). Annealing may also be effected by phase-change (Maddock & Mohanty 1963), or by hydration or dehydration of the crystals. Isothermal hydration or dehydration usually induces a change in retention (Bolton & McCallum 1957, Shankar <u>et al</u>. 1965, Lindner 1958). The rearrangement of the crystal lattice during these processes might facilitate the processes that occur during thermal annealing. It seems that any process that leads to small internal rearrangements of the lattice will have some effect on annealing (Maddock 1975a).

1.3-1 Factors affecting annealing

There are a number of factors that influence the rate and extent of annealing reactions. These reactions are known to be sensitive to the crystal environment of the disintegrating molecule. McCallum and Maddock (1953) demonstrated that, in a series of isomorphous salts such as the permanganates, the rates for annealing were different although the pattern remained the same. Two different crystal modifications of a salt can also behave differently on annealing and even isotopic modifications of the environment may change the rate of annealing (Andersen & Maddock 1963).

Annealing reactions have been shown to be very sensitive to the nature and density of defects present in the solid. It has been observed that even when conditions during irradiation and afterwards were carefully controlled, the reproducibility of measurements from different preparations of a given target material was poor. It soon became evident that the nature and density of crystal defects could influence the retention and the kinetic parameters of the subsequent annealing reactions (Vargas & Maddock 1979).

Ionizing radiation and the crushing of the crystals before neutron irradiation were both found to affect the initial retention and accelerate the subsequent thermal annealing (Maddock & Vargas 1959; Maddock <u>et al</u>. 1963).

It has also been demonstrated that when a neutron-irradiated compound is thermally annealed at constant temperature until the rate of annealing is very slow, and then the crystals are irradiated with ionizing irradiation or crushed, a further stage of rapid annealing takes place (Claridge & Maddock 1961, Andersen & Maddock 1962).

Defects, such as lattice vacancies and dislocations, can provide additional free spaces in the lattice which allow movement of atoms during annealing processes. Some defects can either supply or trap electrons or holes facilitating redox reactions. In some systems the rate of the annealing reaction is influenced by the atmosphere in which annealing is conducted (Nath et al. 1964). A given gas or vapor can also either enhance or inhibit annealing in different neutron-irradiated compounds (Thomas 1972, Rao & Nath 1966).

1.3-2 Features of annealing reactions

Most irradiated systems show some annealing on heating, but this can also occur at very low temperatures (Veljković & Harbottle 1961, Ackerhalt et al. 1969) and at temperatures where decomposition is taking place (Getoff & Maddock 1963, Jach 1968).

An irradiated solid generally contains both the recoil atoms or ions and radioactive atoms combined in ligand-deficient species. Annealing reactions generally involve either reattachment of ligands to reform the parent species or oxidation since the thermalised primary product usually stabilizes in the terminal zone in a lower oxidation state. Sometimes the annealing appears to take place in a single step (Yoshihara & Harbottle 1963, Maddock et al. 1965) and sometimes the reattachment reactions proceed sequentially (Rauscher & Harbottle 1957, Saito et al. 1962).

A remarkable feature of an annealing reaction is its stereospecificity. In cis and trans geometrical isomers or d and l enantiomorphs, annealing usually shows a strong preference for reforming the original configuration of the parent species (Zuber et al. 1961, Dimotakis & Maddock 1961).

Another interesting characteristic is the form of its kinetics. Measurements of annealing are usually made by determining the retention as a function of time and this has already been shown to be independent of the number of radioactive atoms present. This suggests that annealing processes follow simple first-order kinetics. However, the experimental data rarely follow such simple patterns (Shankar et al. 1961, Kudo & Yoshihara 1970). In general, more complex behaviour is observed (Maddock & de Maine 1956). Annealing isothermals show first a rapid rise in retention after which the reaction becomes progressively slower and the curves flatten (the "plateau").

Several models have been proposed to interpret the thermal annealing in neutron-irradiated compounds (Harbottle & Sutin 1959, Maddock & de Maine 1956). The most successful of these assume a set of first-order reactions with a spectrum of energies of activation (Vand 1943, Primak 1955). This model, which can be applied also to exchange reactions in the solid state, is discussed in chapter 2.

The proposition of an exchange model (Harbottle & Sutin 1959) to explain the mechanism whereby the activity could return to the parent form gave impetus to the study of exchange reactions in the solid state. According to this model, the following exchange reaction can take place after neutron irradiation:

$$^{*}X + RX \rightleftharpoons X + RX^{*}$$

where $^{*}X$ is the radioactive atom lying in interstitial positions and RX the parent species.

This model was treated with some scepticism mainly because the activation energy for such a process was thought too high to account for annealing which takes place at moderate temperatures. But the authors argued that "just as the activation energies for diffusion are thought to be lowered in the presence of defects, so may activation energies for exchange".

There now follows an account of the main results of the investigations that followed this proposition.

1.4 Exchange reactions in the solid state

1.4-1 Exchange in doped systems

Isotopic exchange in a solid system was first reported by Kaučić and Vlatković (1963). In their experiment they tried to prove the validity of the exchange model (Harbottle & Sutin 1959) for the annealing of Szilard-Chalmers products. They compared the behaviour of recoil iodine-128 in a sample of calcium iodate irradiated with thermal neutrons, with another sample of the same salt crystallised with traces of radioactive iodide ($^{131}I^{-}$) incorporated in it. The iodide-doped system underwent exchange on heating following kinetics which were very similar to those of the annealing in the irradiated system.

Apers and co-workers (1964) found that thermal treatment of chromic (^{51}Cr)-doped potassium chromate resulted in incorporation of the species having an oxidation state different from that of the parent into the parent chemical form. They named this process "transfer annealing", suggesting that it would involve an oxidation of the tracer species and not necessarily an isotopic exchange. Publication of this work stimulated more interest in this sort of investigation in spite of the practical difficulties in simulating accurately an irradiated system.

Transfer-annealing processes appeared not to be restricted to simple complexes such as the oxyanions. Nath and collaborators observed a transfer of radioactivity occurring in cobalt chelates doped with radio-Co^{2+} which they regarded as arising through genuine isotopic exchange reactions (Nath et al. 1966, Nath & Khorana 1967, Khorana & Nath 1967, 1969).

As interest grew in these reactions, so too did scepticism that isotopic exchange could take place at all in solids. Andersen et al. (1968) suggested that the observed exchange could be an artefact of the analytical techniques used to dissolve the solid sample. This doubt proved to be groundless however; Nath and Klein (1969) observed a solid-state exchange reaction actually taking place using Mössbauer spectroscopy. They doped tris-dipyridil Co(III) perchlorate trihydrate with $^{57}Co^{++}$ and found that, after storage at room temperature for four days, the activity was mainly in the form of $^{57}Co(III)(dipy)_3(ClO_4)_3 \cdot 3H_2O$.

More recent investigations have explored different aspects of these exchange processes, strengthening the evidence that they do indeed take place in the solid state and confirming the resemblance between the annealing and exchange processes. Mahieu et al. (1971) compared the isochronal curves for the exchange reaction in $^{51}Cr(III)$-doped ammonium chromate crystals with those for the neutron-irradiated chromate; he found that the steps in the isochronals for the two samples appeared at the same temperature. He discovered also that, in the doped system, the chemical concentration of Cr(III) remained constant throughout the reaction, providing strong evidence that it had the characteristics of an exchange reaction.

1.4-2 . Factors affecting exchange

Exchange reactions in doped systems and annealing processes have both been shown to be affected by the same factors. They can be enhanced by ionizing radiation, as observed in $^{60}Co^{2+}$ doped-Co(III) $(Acac)_3$(acetylacetonate) and $^{60}Co^{2+}$ doped-Co(III) $(dipy)_3$ $(ClO_4)_3 \cdot 3H_2O$. A similar enhancement occurred on crushing the doped dipyridyl crystals before heating. It was also observed that the rate of exchange in the hydrate form of the doped dipyridyl complex was very much faster than for the anhydrous complex (Nath et al. 1966).

Nath and Khorana (1967) reported an exchange that was stimulated photolytically in $^{60}Co^{2+}$ doped-cobalt chelates.

Exchange processes in the doped systems have been shown to be sensitive to the atmosphere in which the crystals are heated. Exchange in $^{60}Co^{2+}$ doped-tris-dipyridyl cobalt (III) perchlorate trihydrate system is faster in vacuum than in air (Nath et al.

1966) while exchange of $^{58}Co^{2+}$ dopant in a $[Co(C_2O_4)_3]^{3-}$ lattice proceeded faster in air than in vacuum (Kishore & Venkateswarlu 1971). So, too, in exchange processes does the effect of a given atmosphere depend on the system under investigation.

Both annealing reactions and exchange reactions in doped systems have shown stereospecificity (Aalbers & LeMay 1974). They have also demonstrated similar kinetic behaviour.

In view of these similarities, it is now generally accepted that annealing reactions following nuclear changes in solids and exchange reactions are of a similar nature. The differences observed between the irradiated and the simulated systems arise because the different procedures used to prepare each one can lead to different local environments around the impurities, especially in relation to the density and nature of the defects (Maddock 1975b).

1.4-3 Exchange/annealing mechanisms

The role of defects in solid-state reactions and the influence of the atmosphere in which annealing is conducted have both been explored with a view to clarifying the mechanism involved in the exchange/annealing processes.

Maddock et al. (1963) noted the influence of crystal defects on the fate of the recoil atom and the subsequent annealing reactions, and suggested that electrons, holes and excitons may be involved in their mechanisms. Nath et al. (1966) suggested a more elaborate electronic model for exchange/annealing in the solid state. They proposed an exchange mechanism involving participation of free electrons or holes, in view of the fact that ambient electron donors (like acetone and ethyl alcohol) generally accelerate the exchange, while electron acceptors generally retard it (Nath et al. 1966, Rao & Nath 1966, Sarup & Nath 1967, Gutlich & Harbottle 1967). This model may also be invoked to explain the observation that crushing, irradiation with ionizing radiation, compression or other treatment sensitizes the neutron-irradiated and doped systems to subsequent thermal exchange, when electrons or holes are released from traps of variable depth (Nath 1975).

Electrons (holes) can be released during thermal treatment and may electronically excite the dopant/recoil species, triggering exchange with a neighbouring molecule. If the solid substance contains electron donors which can be easily depopulated, then exchange/annealing can take place at relatively low temperatures (Nath 1975). According to this model, the activation energy required for the exchange is derived from the recombination energy of the dopant and a free electron.

The mechanism of the redox step involved in many annealing processes is easily explained in terms of the filling or emptying of traps. In processes where no redox step occurs this might provide local excitation facilitating the annealing / exchange process by ligand transfer (Vargas & Maddock 1979).

The electronic model can also account for the different rates of exchange observed in the hydrated and dehydrated forms of a given compound (Nath 1975).

Further evidence in favour of the electronic model is provided by an elegant experiment combining radiochemical studies and physical measurements of the properties of the crystals.

Andersen and Olesen (1965) demonstrated that the thermal annealing of K_2CrO_4 is associated with the release of trapped electrons or holes by correlating the thermally-stimulated luminescence and conductivity glow peaks with the maxima in the curves for thermal annealing.

Shankar (1968) has proposed an alternative model, suggesting that annealing and exchange result from energy transfer by excitons. According to this view, the migration of excitons and the deposition of their energy at a defect site (such as the location of the recoil or dopant $^*Co^{2+}$) would cause excitation of $^*Co^{2+}$ as well as of a few surrounding molecules. Exchange would then take place between $^*Co^{2+}$ and the cobalt in a chelate molecule yielding the corresponding octahedral $^*Co(II)$ complex. This model can be applied equally well where no redox step is involved (Vargas & Maddock 1979).

Venkateswarlu and collaborators (1969a,b, 1971) have elaborated on Shankar's model to account for the effects of an oxygen atmosphere observed in some cobalt complexes. According to this model, the $^*Co(II)$ complex may transfer an electron to an electron acceptor or it may react with oxygen to form a bridged-type oxygen compound, $^*Co(II)$ complex - O_2 - Co(III) complex, which may subsequently yield the $^*Co(III)$ complex or stabilise to the $^*Co(II)$ state. Maddock (1975b) has criticised this model since it implies the permeability of complexes to oxygen, and in view of the ad-hoc character of the proposed mechanism. Bell and collaborators (1969, 1972) have reported that exchange can proceed via ligand vacancies. They studied the ligand recoil resulting from (n, γ) and (n, 2n) reactions and solid-state exchange reactions in $K_2[R_e X_6]$ where X is F, Cl, Br or I. The radiohalogen activity appeared only in the monosubstituted parent complex form and as a free halogen. According to the authors, substantial formation of the monosubstituted species can be the result of reaction between the recoil halogen and either intact hexahalogene-anions or those that have lost only one ligand. They also observed that in both radiohalide-doped complexes and in neutron-irradiated complexes, thermal treatment promoted the entry of the dopant or recoil halides into the ligand sphere, these processes being very similar.

The authors concluded that the reaction proceeded via ligand vacancies for the following reasons: (i) the energy required for a one-step direct replacement reaction is higher than would be available from thermal treatment; (ii) the solid-state exchange was not affected by electronic defects introduced by ionizing irradiation prior to thermal treatment.

The proposed mechanism for thermal annealing and isotopic exchange was:

1. Ligand-vacancy formation:

$$[Re\ X_6]^{2-} \rightleftharpoons [Re\ X_5\ \square]^- + X^-$$

2. Ligand-vacancy migration:

$$[Re\ X_6]^{2-} + [Re'\ X_5\ \square]^- \rightleftharpoons [Re\ X_5\ \square]^- + [Re'\ X_6]^{2-}$$

3. Nucleophilic substitution by radiohalide:

$$[Re\ X_5\ \square]^- + {}^*X \longrightarrow [Re\ X_5\ {}^*X]^{2-}$$

When sufficient vibrational energy is available, a primary ligand vacancy which is either already present in the complex or was formed by thermal dissociation, interacts with the nearest ligand of a neighbouring molecule, so that the vacancy migrates. When such a vacancy migrates near a dopant or recoil atom, it will be filled by that atom.

Despite the considerable amount of experimental data and the various mechanisms that have been proposed to explain them, Maddock (1975b) has stated that there is still not a well-defined mechanism for exchange/annealing processes in the solid state.

The study of exchange reactions between normal lattice species has emerged as a new area of investigation where new information about exchange mechanisms in the solid state can be obtained. Systems where the exchanging atoms occupy normal lattice positions in the crystal in comparable concentrations can be used to study the exchange reactions on the assumption that they are homogeneous reactions taking place in the whole crystal. Disadvantages of doped systems, such as the great disparity in concentration between the reactants and the doubtful nature and location of one of the reacting species, disappear in the case of exchange between normal lattice occupants.

1.4-4 Exchange between normal lattice species

Very few experiments have been reported so far on solid-state isotopic exchange reactions between two normal lattice species.

The first attempt investigated the exchange between coordinated and ionic halogen atoms in the solid phase in compounds such as bromopentammine complexes of rhodium and iridium (Schmidt & Herr 1965) and in a series of dihalo-bis (ethylenediamine) Co-complexes (Schmidt & Rössler 1966). While the halogen atoms exchange only very slowly in the bromopentammine complexes, the exchange takes place relatively rapidly in the second series of compounds. Irradiation of trans-$[Co(en)_2{}^{*}Cl_2]$ Cl with X or γ rays increased the rate of exchange. It was also discovered that the irradiated samples showed a more rapid increase in exchange rate with increasing temperature than the untreated samples. These results suggested that exchange may take place by species jumping into lattice defects.

No further experiments were carried out until 1975 in spite of the hope that "this information on the unexpectedly high mobility in the lattice will throw some more light on the observed effects following nuclear transformations" (Schmidt & Herr 1965). In that year, the Lazzarinis (Lazzarini & Fantola-Lazzarini 1975) investigated the exchange between Co atoms in the compound $[Co\ (H_2O)_6][Co\ EDTA]_2.4H_2O$. The isotopic exchange occurred simultaneously with the dehydration of the compound. The exchange could also be initiated thermally after γ-irradiation of the crystals and it was observed that the exchange between the Co atoms approached its equilibrium value with the increase in temperature, but it ceased as soon as the anionic vacancies produced by irradiation were annealed by the heating. The Lazzarinis concluded that exchange took place via vacancies rather than by motion in a ring of two cobalt atoms.

Another compound investigated by the same authors (Lazzarini and Fantola-Lazzarini 1976) was $[Co\ (H_2O)_6][Co\ glyc_2\ (NO_2)_2]_2$. In this system, exchange begins with dehydration and above 130°C it is correlated with the decomposition of the compound. The isotopic exchange appeared to reach its equilibrium condition under γ-ray irradiation, observations that led the authors to conclude that exchange under normal conditions has a negligible probability of taking place. The exchange can only occur if the concentration of vacancies attains a certain value or while the crystal lattice is highly excited by γ-ray absorption or is undergoing transformations such as dehydration or decomposition.

An exchange reaction between the thallium atoms in the mixed-valence compound $Tl(I)_3\ Tl(III)\ Cl_6$ was reported by Fernandez Valverde et al. (1978). They observed that crushing the crystals before heating greatly accelerated the exchange process, but that it was not affected by ionizing radiation. In such a mixed-valence system exchange could be expected to occur by a purely electronic process induced by ionizing radiation. As this was not observed experimentally the authors suggested an exchange process involving physical interchange of Tl atoms. Thermal treatment of a neutron-irradiated sample showed identical behaviour to that observed in the labelled system (Fernandez Valverde & Duplatre 1977).

More recently the mixed-valence system caesium chloroantimonate complex $Cs_4\ Sb(III)\ Sb(V)\ Cl_{12} - 2Cs_3\ Sb(III)\ Cl_6$ has been studied (Nyarku 1978). Exchange between Sb(III) and Sb(V) was observed in the temperature range 60° - 140°C. Gamma and UV irradiation did not produce appreciable exchange but did enhance the subsequent thermal exchange process. The possibility of inter-valence electron transfer playing a part in the processes leading to exchange in this system was suggested. Nyarku (1978) also investigated the exchange between Ni atoms in the compound $[Ni(H_2O)_6][Ni(CN)_4]$. In this system exchange takes place at reasonably low temperatures (27-60°C). Samples heated in air or under vacuum displayed similar characteristics, showing no sensitivity to the ambient atmosphere. Increasing doses of γ-irradiation enhanced the post-irradiation exchange processes and crushing the crystals had no effect upon exchange.

A diffusion process involving some movement of the species in the compound was suggested to account for the observed exchange. Such a process would be enhanced by the structural modifications that occur during the dehydration of the compound.

These are the few cases of exchange of normal lattice species in solids that have been reported to date. Although some progress has already been made, there is a need for more studies on the mechanisms of such processes.

The present investigation, where the solid-state isotopic exchange reactions between normal lattice species is studied, was proposed with a view to obtaining more information on the nature and mechanisms of this type of solid-state exchange reaction.

CHAPTER 2 - SOLID-STATE EXCHANGE REACTIONS

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2.1 Solid-state reactions

A solid-state chemical reaction occurs when local transport of matter is observed in crystalline phases. Solid-state reactions may be classified as follows:

1. Homogeneous reactions.
2. Reactions in single-phase inhomogeneous systems.
3. Heterogeneous reactions.

A homogeneous reaction occurs through a local rearrangement of structural elements. Reactions in single-phase inhomogeneous systems take place in phases where local fluxes of the structural elements occur, leading to local variations in composition, while heterogeneous reactions are characterized by the occurrence of phase boundaries across which mass transport takes place (Schmalzried 1974). Isotopic exchange reactions between normal lattice species belong to the class of homogeneous solid-state reactions.

The transport of matter in the solid is dependent upon the mobility of the individual particles in the lattice. In a perfect crystal, motion of the individual particles from their lattice sites cannot occur; every case of mass transport in solids is therefore directly dependent upon deviation from ideal crystalline order. Consequently, when dealing with reactions in solids, we are always concerned with the role that the defects play. The presence of defects confers on the crystal characteristics that make reaction possible. These include the possibility of movement of atoms or ions resulting in the transport of matter, localized regions of effective electrical charge and localized stress fields.

In order to understand any chemical reaction in the solid state, it is necessary to know about the nature and properties of defects in solids. It is now therefore presented a classification of those defects normally encountered in a crystal, a description of their specific properties and some techniques by which they may be introduced into perfect crystals in the laboratory.

2.1-1 Defects in solids and their effects on solid-state reactions

Finite crystals at temperatures above 0^{o}K exhibit different types of defects which can be described as follows:

1. Point defects
   - (i) Vacant lattice sites
   - (ii) Interstitial atoms or ions.
   - (iii) Impurity atoms or ions in proper lattice sites or in interstitial positions.
2. Line defects
   - (i) Edge dislocations
   - (ii) Screw dislocations
3. Elementary excitations
   - (i) Free electrons
   - (ii) Positive holes
   - (iii) Excitons
   - (iv) Phonons

The solid surface itself can be included as a defect because its presence in a solid implies a discontinuity in the material and electrical properties of the crystal. More complex defects can always be analysed into combinations of these primary defects. For example an anion vacancy can combine with a cation vacancy to form a Schottky defect, while the association of a vacancy with an interstitial forms a Frenkel defect. Several other defect complexes, such as point defects associated with dislocation lines, can also occur within a solid (Rees 1964a).

The presence of point defects in a crystal cause distortion of the crystalline structure in the immediate vicinity of the defect. This change introduces local stress fields and a local redistribution of effective electrical charges. Cation vacancies carry negative charges and anion vacancies positive charges; hence the resultant field of a defect is able to trap charge carriers and any other mobile defects that have different charges from the normal lattice occupants. It is through point defects, in the absence of others, that the movement of atoms and ions can take place in a crystal (Rees 1964a) and this results in the net transport of matter.

Dislocations influence the creation, annihilation, aggregation and movement of point defects and elementary excitations. When they occur in ionic crystals they usually have a net charge because of the different energies required to create anion and cation vacancies. An excess of anion vacancies around a dislocation will cause it to have a net positive charge, enabling it to trap electrons; similarly dislocations carrying net negative charges are expected to trap positive holes.

Sites of lower potential energy are created along dislocations due to the displacement of atoms or ions from their equilibrium position. Consequently there is a tendency towards accumulation of point defects in its neighbourhood. Dislocations may also act as paths along which diffusion may easily take place in a crystal (Rees 1964b).

The role of elementary excitations in solid-state reactions is related to the transfer of charge, thermal energy and electronic excitation through the crystal. Charge can be transferred by means of electrons and positive holes. These charge carriers form complexes when they are trapped by point defects. An electron can readily be trapped in an anion vacancy forming an F-centre; a positive charge can be trapped in a cation vacancy forming a V-centre (Spinks & Woods 1964). Thermal energy, on the other hand, is transferred through the solid by means of phonons, while electronic excitations travel by means of excitons, (Maddock et al. 1963).

Defects must be present in high concentrations if their influence on solid-state reactions is to be measured. There are a number of convenient techniques by which their concentration may be increased above the thermal-equilibrium level. Ionizing radiation may be used to generate free electrons or holes; ultraviolet light (~ 10 eV), X-rays (10-100 KeV), γ-rays (1.25 MeV) and high-energy electrons (100 $\overset{K}{\underline{\text{k}}}$eV - 10 eV) are all examples of ionizing radiation (Henderson 1972).

In an ionic lattice the incident radiation strips a negative ion off some electrons. The ionized anionic species, now positively charged and surrounded by positively-charged nearest neighbours, will be displaced into interstitial sites by the high repulsive force. The stripped electrons move through the crystal and may produce further ionization or may be trapped by anion vacancies (Varley 1954).

The concentration of point defects increases rapidly with increasing temperature. It may be increased over its equilibrium value by rapid cooling or quenching from a high temperature. Quenching is more likely to produce vacancies than interstitials as the energy required for the former is generally lower than that for the latter (Henderson 1972).

Dislocations may be introduced if accidents occur during the growth of a crystal or if the crystal is crushed. Interactions between dislocations will generate appreciable quantities of lattice defects, vacancies and interstitials (Billington & Crawford 1961).

2.2 Isotopic exchange

An isotopic exchange is a spontaneous and reciprocal substitution of an atom in a molecular entity by another atom of the same atomic number, arising from the same or another molecular entity.

A system labelled with a radioactive isotope is considered to be chemically homogeneous. Then if the initially labelled species contains x radioactive atoms and y inactive isotopic atoms, and if after exchange x' radioactive atoms exchange, it can be concluded that y' inactive atoms have also exchanged. This approach has been successfully used to investigate problems of chemical bonding structure, reaction mechanisms, etc. (Haissinsky 1964).

As it is assumed that isotopes are chemically identical, and since the initial and final states of the exchanging system are the same, then the variation of entalpy, ΔH, is nearly zero for any isotopic exchange reaction. However there is a variation in the free energy of the system resulting from the increased entropy due to the redistribution of the radioactive indicator. The true energy of the system decreases by an amount calculated from the entropy change as follows:

$$\Delta G = - T \ \Delta S$$

where ΔG is the change in the free energy, and ΔS is the change in the entropy.

All other free-energy changes should in principle be zero. This implies that the transfer of matter during the exchange process is bidirectional and is therefore not associated with a net chemical change.

Isotopic exchange reactions often require an activation energy which is usually provided by thermal agitation; they may be accelerated, however, by the action of light, ionizing radiation or other means (Haissinsky 1964).

From the kinetic point of view, exchange reactions can be divided into homogeneous and heterogeneous types, i.e. exchange reactions occurring between reactants uniformly distributed in a single phase or in different phases, respectively. Only the kinetics of homogeneous exchange reactions will be considered here since the exchange between two normal lattice species in solid state systems is of this type.

2.3 The kinetics of homogeneous exchange reactions

When an exchange reaction takes place in a homogeneous system, it does so between reactants that are uniformly distributed in the same phase and all conditions, except the distribution of radioactive atoms between reactants, remain constant during the reaction.

Homogeneous exchange reactions are first-order with respect to time, irrespective of the mechanism by which they occur, the number of exchangeable atoms in each species so long as all show the same energy of activation, or the concentration of the radioactive atoms used as indicators. The reason for this particularly simple result is that the composition of the reacting system remains chemically unchanged throughout the reaction (McKay 1938).

The law for homogeneous exchange reactions has the form

$$\ln(1-F) = -\lambda t \tag{2.1}$$

commonly known as the McKay equation (McKay 1938). The derivation of this law and the definition of F, the "fraction of exchange" are given in Appendix 1.

λ has the form:

$$\lambda = R\,\frac{(a+b)}{ab} \tag{2.2}$$

where a and b are the concentrations of the exchanging species and R is the rate of exchange. R depends on the order of the reaction for each component of the system as follows:

$$R = k\,a^{\alpha}\,b^{\beta} \tag{2.3}$$

where k is the rate constant of the form

$$k = \upsilon\,e^{-E_a/\kappa T} \tag{2.4}$$

where υ is a constant frequency term, E_a is the energy of activation, κ is Boltzmann's constant and T is the temperature.

The exchange processes observed in solid systems usually do not obey the simple rate law for exchange expressed by this equation. A semi-logarithmic plot of (1-F) against t of the data for an exchange isothermal usually does not show a straight line, the exchange proceeding more slowly at longer times. These "exchange isothermals" closely resemble the annealing isothermals obtained for neutron-irradiated solid systems.

When considering a solid system, the possibility that there may be one or more reaction paths with different activation energies and probabilities should be taken into account. Thus path i, with frequency factor υ_i, and activation energy E_{ai}, is supposed to apply to a fraction p_i of the sites. For each of these sites the rate constant is

$$k_i = \upsilon_i \, e^{-E_{ai}/\kappa T} \tag{2.5}$$

The total unexchanged fraction is then

$$(1-F) = \sum_i P_i \, e^{-\lambda_i t} \tag{2.6}$$

The whole process is therefore the result of two or more reactions in the solid, and it displays a spectrum of activation energies and/or frequency factors.

In practice it is not possible to establish both the distributions in E_a and υ from one set of kinetic data. Usually υ is taken as constant in which case equation (2.5) becomes

$$k_i = \upsilon \, e^{-E_{ai}/\kappa T} \tag{2.7}$$

The spectrum of activation energies may then be found from equation (2.6) by numerical solution, fitting the data obtained during the course of a reaction at different times and different temperatures to the model described above. It may also be extracted from the shapes of the experimental curves themselves. This method, which has been applied to many types of annealing processes, is presented in the next section, together with a treatment of the kinetics of processes with distributed energies of activation.

2.4 Processes with distributed energies of activation or frequency factors

Maddock (1975a) has given a detailed treatment of the kinetics of annealing processes with distributed energies of activation or frequency factors. He has also analysed the merits of these processes when applied to data from isothermal, isochronal or other types of treatment.

Analysis of the kinetic data on many kinds of annealing reactions in terms of a single process, so that the rate law can be expressed as

$$\frac{dn}{dt} = - kn^{\gamma} \tag{2.8}$$

where n is the number of annealable centres, k is the rate constant and γ is the order of reaction, yields very high values of γ with doubtful physical significance. However, if a spectrum of energies of activation is assumed, more satisfactory values of one or two for γ will be obtained.

Although either or both of υ and E_a may show a distribution of values it is not usually possible in practice to establish them both from one set of kinetic data (Kimmel & Uhlmann 1969).

In what follows, it will be assumed that the frequency factor is constant and that there is only a distribution of activation energies, since it has yet to be shown that experimental data are better treated by another method.

2.5 First-order processes with distributed energies of activation

In a single, first-order annealing process, with constant ν and E_a, the number, n, of reactive entities and the rate of the reaction at time t can be expressed in terms of n_o, the initial number of reactive entities. The unreacted fraction is given by

$$\frac{n}{n_o} = e^{-kt} \qquad (2.9)$$

with $k = \nu e^{-E_a/\kappa T}$.

Then, $$n = n_o \exp\left[- \nu\, t.\exp\,(-E_a/\kappa T)\right] \qquad (2.10)$$

and $$\frac{dn}{dt} = - kn \qquad (2.11)$$

so that $$\frac{dn}{dt} = -n_o\ \nu \exp\,(-E_a/\kappa T).\ \exp\left[-\nu\, t \exp\,(-E_a/\kappa T)\right] \qquad (2.12)$$

The spectrum of energies of activation at time t = 0, can be represented by a distribution function with derivative $f'(E_a)$ such as

$$dN_o = f'(E_a)dEa$$

where dN_o is the initial number of unreacted centres with energies of activation lying between E_a and $E_a + dE_a$, and $N_o = \int_0^\infty f'(E_a)dE_a$. For such a spectrum one obtains

$$\frac{dN}{dt} = - \int_0^\infty \nu \exp(-E_a/\kappa T).\exp[-\nu t \exp(-E_a/\kappa T)].f'(E_a)dE_a \qquad (2.13)$$

and

$$N = \int_0^\infty \exp[- \nu t \exp(-E_a/\kappa T)].f'(E_a)dE_a. \qquad (2.14)$$

For many purposes, especially where a property proportional to N is measured such as the retention (the fraction of reacted centres, $R = \left(1 - \frac{N}{N_o}\right)$, it is convenient to normalize $\int_0^\infty f'(E_a)dE_a$ to unity and obtain $F'(E_a)$, the normalized distribution function.

The unreacted fraction, θ, is then given by

$$\theta = \frac{N}{N_o} = \int_0^\infty \exp[-\upsilon t \exp(-E_a/\kappa T)].F'(E_a)dE_a. \qquad (2.15)$$

Similarly

$$\frac{d\theta}{dt} = -\int_0^\infty \upsilon \exp(-E_a/\kappa T) \exp[-\upsilon t \exp(-E_a/\kappa T)].F'(E_a)dE_a. \qquad (2.16)$$

2.5-1 Isothermal annealing data

The experimental data from isothermal measurements yield $\theta(t)$. The annealing function, defined as

$$\phi(E_a,t) = \exp[-\upsilon t \exp(-E_a/\kappa T)], \qquad (2.17)$$

gives the fraction of unreacted species present at time t for given E_a, T and υ. If we suppose now that t, T and υ are constant, the function ϕ will give the fraction of unreacted species for different values of E_a. Figure 2.1 shows the form of ϕ plotted as a function of E_a for $\upsilon = 10^{10}s^{-1}$; E_a is expressed in units of kT. The function has a point of inflexion where $E_a = E_{ao}$ and $\left(\frac{\partial\phi}{\partial E_a}\right)_t$ is a maximum.

Since $\left(\frac{\partial\phi}{\partial E_a}\right)_t = \frac{-t}{\kappa T}\left(\frac{\partial\phi}{\partial t}\right)_{E_a}$, the entities with energy of activation E_{ao} anneal the most quickly.

Putting $\left(\frac{\partial^2\phi}{\partial E_a^2}\right)_t = 0$

gives $E_{ao} = \kappa T \ln \upsilon t.$

A graphical representation of the progress of the annealing in terms of the movement of the annealing function across the energy spectrum, expressed in terms of ϕ and $F'(E_a)$ is represented in figure 2.2. As t increases, the ϕ function moves across the

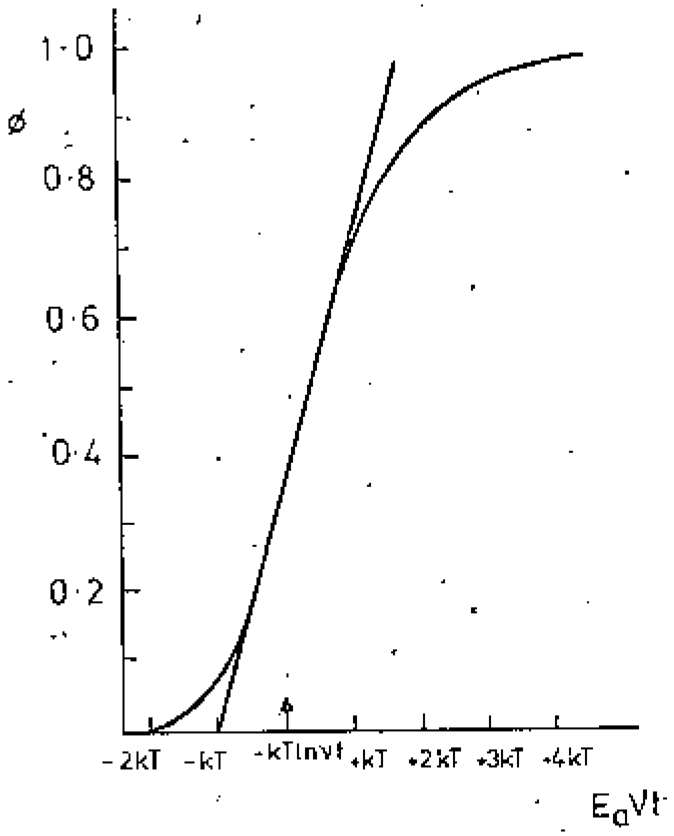

Fig. 2:1 The annealing function, ϕ, for a first-order process over the range of energies of activation $[kT\ln\nu t + 4kT]$ to $[kT\ln\nu t - 2kT]$. The tangent at the point of inflection is shown (Maddock 1975).

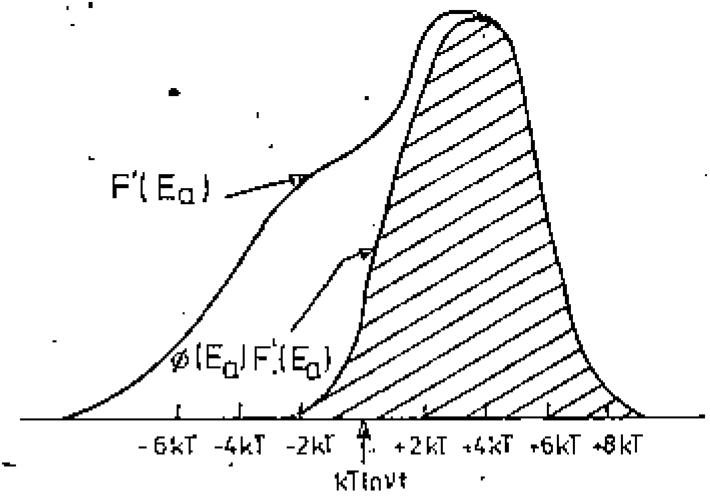

Fig. 2.2 Modification of $F'(E_a)$ as annealing proceeds. The cross-hatched area shows the unannealed portion (Maddock 1975).

energy spectrum towards higher energies. Its position defines, at a given time t, the curve $\phi(E_a)F'(E_a)$; the unannealed fraction, $\int_0^\infty \phi(E_a)F'(E_a)dE_a$, is represented by the hatched area in the figure. The portion of the initial spectrum to the left of ϕ (i.e., at activation energies lower than E_{ao}) has already been annealed out while the portion to the right has yet to be annealed.

$F'(E_a)$ can be extracted from the experimental data $\theta(t)$ by means of the simple approximation suggested by Vand (1943) and extended by Primak (1955, 1960). It is assumed that the annealing function ϕ can be approximated by a step (Heaviside) function located at $E_{ao} \approx \kappa T \ln \nu t$ ($\phi = 0$, $E_a < \kappa T \ln \nu t$; $\phi = 1$, $E_a > \kappa T \ln \nu t$). This approximation is valid only if the spectrum of energies of activation extends over an interval of many κT, and $F'(E_a)$ is constant, or nearly so, over the range of E_a undergoing active annealing.

Then

$$\theta(t) = \int_0^\infty F'(E_a)\phi(E_a,t)dE_a \approx \int_0^\infty F'(E_a)H(E_a-E_{ao})dE_a \qquad (2.18)$$

$$\theta(t) \approx \int_{E_{ao}}^\infty F'(E_a)dE_a \qquad (2.19)$$

and $$\frac{d\theta}{dt} \approx -F'(E_a)\frac{dE_{ao}}{dt} . \qquad (2.20)$$

But $E_{ao} = \kappa T \ln \nu t$

and $\dfrac{dE_{ao}}{dt} = \dfrac{\kappa T}{t}$.

Therefore $$F'(E_{ao}) \approx -\left(\frac{t}{\kappa T}\right)\frac{d\theta}{dt} \qquad (2.21)$$

or $$F'(E_{ao}) \approx -\left(\frac{1}{\kappa T}\right)\frac{d\theta}{d\ln t} . \qquad (2.22)$$

From plots of θ against $\ln t$, the slopes $\dfrac{d\theta}{d\ln t}$, may be measured at various values of t and on different isothermals. Hence values of $F'(E_{ao})$ at different t and T may be obtained. A plot of these values of $F'(E_{ao})$ against $E_{ao} = \kappa T \ln \nu t$ will give a reasonably good representation of the distribution of activation energies.

However, to evaluate E_{ao} one must know ν. If a set of isothermals has been measured at small enough intervals of temperature (say, $\Delta T = 0.1\ T$), many pairs of points (t_1,T_1), (t_2, T_2), will be obtained for which $F'(E_{ao})$ has the same value. If the values of θ are nearly the same for each member of the pair and $F'(E_a)$ is not multivalued in E_a within one or two units of κT around E_{ao}, then

$$(\ln \nu + \ln t_1)\ \kappa T_1 = (\ln \nu + \ln t_2)\ \kappa T_2$$

or

$$\ln \nu = (T_2 \ln t_2 - T_1 \ln t_1)/(T_1 - T_2). \qquad (2.23)$$

From several pairs of points a "best" value of ν can be defined. Since $\kappa T \ln \nu t = E_{ao}$,

$$\left(\frac{\partial \ln t}{\partial T} \right)_{E_{ao}} = - \frac{E_{ao}}{\kappa T^2}, \qquad (2.24)$$

which relates t and T in the corresponding pairs (t_1,T_1), (t_2,T_2), etc.

Also

$$-\left(\frac{1}{\kappa T} \right) \frac{d\theta}{d \ln t} = F'(E_{ao}). \qquad (2.25)$$

$$\therefore \qquad \left[\frac{d}{dT} \cdot \left(\frac{d\theta}{d \ln t} \right) \right]_{E_{ao}} = \kappa F'(E_{ao}) \qquad (2.26)$$

showing that the slopes of the $\theta - \ln t$ plots are proportional to T at corresponding points.

It follows from the above relations that a set of isothermals plotted as $\theta - \ln t$ can be made to overlap on one curve by appropriate displacement along $\ln t$ axis. The earlier portions of the isothermals at higher temperatures should have values of θ which overlap the isothermals of lower temperature at longer times. The best value of ν will give the best overlap between successive isothermal annealing curves.

In this manner, $F'(E_a)$ may be deduced from the experimental curves. These results must, however, be regarded as approximate since the mathematical treatment involves approximations and because of experimental errors (McKay 1971). In view of the precision of both the data and the resolution of the Vand-Primak analyses (ca ± 2 κT), "lines" in the spectrum of energies of activation will only be resolved reliably when they are separated by more than about 2 κT. A closely-spaced line spectrum cannot be distinguished from a continuous distribution over the energy interval (Vargas & Maddock 1979).

2.5-2 Isochronal annealing data

The distribution function can also be obtained from isochronal data. In this case the annealing is measured after a fixed time interval at different temperatures. The experimental data yields $\theta(T)$ and can be treated in a similar fashion to the isothermal data.

The annealing function is

$$\phi\,(E_a T) = \exp\left[-\nu t \exp\left(-E_a/\kappa T\right)\right] \qquad (2.27)$$

and

$$\left(\frac{\partial\phi}{\partial T}\right)_{E_{a\phi}} = -\left(\frac{E_a}{T}\right)\left(\frac{\partial\phi}{\partial E_a}\right)_T. \qquad (2.28)$$

There is a point of inflexion in ϕ such that

$$E_{ao}\left[1 - \nu t \exp(-E_{ao}/\kappa T)\right] \doteq 2\kappa T \qquad (2.29)$$

Approximating as before gives

$$\theta = \int_0^\infty F'(E_a)\, \phi(E_a,T)\, dE_a \qquad (2.30)$$

and therefore

$$\frac{d\theta}{dT} = \int_0^\infty F'(E_a) \frac{d\phi}{dT} dE_a = - \int_0^\infty F'(E_a) \frac{E_a}{T} \frac{d\phi}{dE_a} dE_a \qquad (2.31)$$

or

$$\frac{d\theta}{dT} \approx F'(E_{ao}) \frac{E_{ao}}{T} \qquad (2.32)$$

and

$$F'(E_{ao}) = - \left(\frac{1}{E_{ao}} \right) \frac{d\theta}{d\ln T} \qquad (2.33)$$

The resolution will be the same as for isothermal data but this method offers some advantages in the fact that fewer measurements are needed and in the fact that the structure of the distribution function $F'(E_a)$ is more apparent from the $\theta(T) - \ln T$ plots.

2.5-3 Application of the model to annealing following nuclear changes and to isotopic exchange in solids

The models proposed to fit the data obtained from annealing processes following nuclear changes, which were based on correlated diffusion - controlled kinetic expressions and on recrystallization laws, proved not to be very successful (Harbottle & Sutin 1959, Maddock & de Maine 1956).

Better fits to the annealing data were obtained when spectra of energies of activation were assumed for first-order processes.

In spite of this, however, there is some evidence suggesting that the theory is not complete. The experimental data show that, for long annealing times at constant temperature, the reaction slows down too much and, in consequence, the best value of the frequency factor, ν, does not give a complete overlap of adjacent isothermals. This suggests that it is not only E_a that varies but that some changes in υ occur also, or $F'(E_a)$ changes on heating (Maddock 1975a). Nevertheless with the Vand-Primak analysis a more quantitative expression can be given to the influence of the different factors that affect the annealing process. It has been shown that defects introduced by different treatments of the neutron-irradiated crystals displace the $F'(E_a)$ distribution toward lower energies (Costea & Negoescu 1965, Costea & Podeanu 1968).

The experimental data for exchange processes in the solid state have also been shown to be fitted best by a model assuming a distribution of activation energies for first-order processes. It is already established that exchange reactions in doped systems and annealing processes have similar kinetics. There is little information at present on the kinetics of exchange between two normal lattice species; however, in the few cases reported to date, the experimental data are fitted well by such a model.

It was found that for the $Tl(I)_3Tl(III)Cl_6$ mixed-valence system (Fernandez Valverde <u>et</u> <u>al</u>. 1978), the kinetics of the exchange between Tl(I) and Tl(III) is compatible with three first-order processes, each with different energy of activation. It was also observed that the fraction which exchanged via the path of lowest energy of activation was markedly increased on grinding the crystals before heating.

In the compounds $[Ni(H_2O)_6][Ni(CN)_4]$ and $Cs_4Sb(III)Sb(V)Cl_{12}-2Cs_3Sb(III)Cl_6$ (Nyarku 1978), the experimental data were better characterised by three energies of activation. Within the N_i compound, it was observed that irradiation by gamma and UV photons lowered further the activation energies of those processes which already had the lowest energies, and that their proportion was increased. By contrast, crushing of the crystals before heating altered the energies of the high-energy processes in the Sb system, besides affecting the proportions of all the reactions going via paths of different energy.

CHAPTER 3 - EXPERIMENTAL METHODS

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CHAPTER 3 - EXPERIMENTAL METHODS

The compounds listed below were synthesised in order that their suitabilities for use in studies of solid-state isotopic exchange reactions between normal lattice species could be determined. Such compounds need to contain a given element either in two different coordination sites or in different oxidation states, or both. There are many references to this sort of compound in the literature; see for example the review and classification of the mixed-valence inorganic systems by Robin and Day (1967).

The following compounds were chosen:

(i) $Hg[Hg\,EDTA].xH_2O$ - mercury (II)-ethylenediaminetetra-acetatomercurate (II) hydrated;

(ii) $Fe[Fe(CN)_5NO].xH_2O$ - iron (II)-pentacyanonitrosylferrate (III) hydrated;

(iii) $KFe[Fe(CN)_6].xH_2O$ - soluble Prussian Blue;

(iv) $[Fe(H_2O)_6][Fe\,EDTA(H_2O)]_3.xH_2O$- hexaaquoiron (III)-aquoethylenediaminetetraacetatoferrate (III)monohydrated;

(v) $[Co(NH_3)_5Cl]Cl_2$ - chloropentamminecobalt (III) chloride;

(vi) $Cr_2(C_2O_4)_3.6H_2O$ - chromium (III) oxalates:

  a) $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ - hexaaquochromium (III) trioxalatochromate (III);

  b) $[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$ - monooxalate tetraaquochromium (III) - dioxalatodiaquochromate (III).

This chapter deals with the methods of synthesis, labelling and analysis, specification of the different treatments given to the labelled samples and the counting techniques. I leave the investigation of the suitability of these compounds for exchange studies until the next chapter.

3.1 $Hg[Hg\text{-}EDTA].xH_2O$ - mercury (II) - ethylene diaminetetra-acetatomercurate (II) hydrated

The possibility of synthesis of $Hg[Hg\ EDTA].xH_2O$ came from the work done by Brintzinger and Munkelt (1948) who obtained the complex acids of Sr, Ba, Bi and Hg with EDTA and some of its salts, where EDTA refers to ethylenediaminetetra-acetate.

3.1-1 Preparation

The preparative procedure used was based on the following reaction:

$$(CH_3COO)_2Hg + H_2[Hg\ EDTA].H_2O \rightarrow Hg[Hg\ EDTA].xH_2O + 2\,CH_3COOH$$

The complex acid, $H_2[Hg\ EDTA].H_2O$, was obtained by the slow addition of mercuric oxide to a boiling solution of ethylenediaminetetracetic acid, following the method of Brintzinger and Munkelt (1948).

The compound $Hg[Hg\ EDTA].xH_2O$ was prepared by the addition of a solution of mercuric acetate, gradually and with constant stirring, to a suspension in water of the complex acid $H_2[Hg\ EDTA].H_2O$. After 30 min of stirring, the resulting precipitate was filtered, washed with water and dried under vacuum at room temperature. The product was a fine white crystalline powder insoluble in water.

This preparation was conducted at room temperature to minimise exchange during the synthesis of the compound.

3.1-2 Labelling

Hg [Hg EDTA].xH_2O was labelled with ^{203}Hg in the cationic site of the compound. The radioisotope ^{203}Hg was supplied by the Amersham Centre as mercuric acetate in aqueous solution containing 2.31 mg Hg/ml; it had an activity of 2.05 mCi in a total volume of 1 ml. This solution was diluted and a measured volume was added to a solution of mercuric acetate. The result was used in the preparation of the labelled compound, following the procedure described in section 3.1-1. The specific activity of the labelled compound was 0.05 µCi/mg.

3.1-3 Analysis

The mercury content was determined volumetrically by titration with thiocyanate after destruction of the complex with concentrated acid (Hillebrand <u>et al</u>. 1953, Bordeianu 1935).

The percentage of Hg found was 55.36 ± 0.34% indistinguishable from the theoretical value of 55.30%, appropriate to the formula Hg [Hg EDTA].2H_2O.

A loss of weight corresponding to two molecules of water was observed when a sample of the compound was dried in a drying pistol, at 50°C, under vacuum.

The compound was unstable against high temperature, changing colour and starting to decompose when heated to 110°C.

The contents of carbon, hydrogen and nitrogen were determined by microanalysis. The results agree well with the theoretical values corresponding to the formula Hg [Hg EDTA].2H_2O, as shown in the following table:

		found (%)	calcd. (%)
C	–	16.73	16.56
H	–	2.11	2.22
N	–	3.89	3.86

3.2 Fe $[Fe(CN)_5NO].xH_2O$ – iron (II)-pentacyanonitrosylferrate (III) hydrated

3.2-1 Preparation

The compound Fe $[Fe(CN)_5NO].xH_2O$ was first synthesised by Playfair (1850) by adding a 2% solution of ferrous sulphate to a 10% solution of a soluble nitroprussiate, with constant stirring.

The same method, described by the following equation was used:

$$FeSO_4.7H_2O + Na_2[Fe(CN)_5NO].2H_2O \longrightarrow$$

$$\longrightarrow Fe[Fe(CN)_5NO].xH_2O + Na_2SO_4 + H_2O$$

The precipitate was separated by filtration, washed with water and dried under vacuum at room temperature.

$Fe[Fe(CN)_5NO].xH_2O$ is a powder with a salmon-pink colour. It is almost insoluble in water. The colour of the compound changes to green when exposed to sunlight; $[Fe(CN)_5NO]^{2-}$ changes gradually to Berlin blue, HCN and NO under the action of direct sunlight (Swinehart 1967). In view of this, the preparations were carried out in the dark.

3.2-2 Labelling

The active compound was synthesised with ^{59}Fe introduced into the cationic side.

^{59}Fe was supplied by the Amershan Centre, as $^{59}FeCl_3$ in 0.1 M HCl, containing 9.5 µg Fe/ml and having an activity of 500 µCi in a total volume of 5 ml.

An aliquot of 2 ml of the radioactive solution was diluted to 50 ml with water and ^{59}Fe(III) was reduced to ^{59}Fe(II) by SO_2 gas bubbled through the solution as it was gradually heated to boiling. The excess of SO_2 was removed by a stream of CO_2 and the solution left to cool in an atmosphere of CO_2 (Vogel 1961).

^{59}Fe(II) was then added to an inactive 2% solution of ferrous sulphate. The labelled compound was prepared from this following the procedure described in section 3.2-1. The specific activity of the labelled compound was 0.02 µCi/mg.

3.2-3 Analysis

A sample was prepared for analysis by decomposion by fusion with concentrated H_2SO_4 and $KHSO_4$. The iron content was then determined volumetrically with potassium dichromate, after reduction of iron (III) to iron (II) with stannous chloride solution (Vogel 1961).

The extent of hydration was determined by the loss of weight measured in samples heated either in an oven at 100°C, or in a drying pistol at 85°C under vacuum. In each case the loss of weight corresponded to five molecules of water, in agreement with Salvadeo (1959).

The contents of carbon and nitrogen were determined by microanalysis. The results agreed well with the theoretical values corresponding to the formula $Fe[Fe(CN)_5NO].5H_2O$, as shown in the following table:-

		found (%)	calcd. (%)
Fe	-	30.92 ± 0.31	30.85
C	-	16.82	16.60
N	-	23.33	23.22

3.3 K Fe $[Fe(CN)_6]\cdot xH_2O$ - soluble Prussian Blue

3.3-1 Preparation

Soluble Prussian blue was prepared by mixing 1:1 molar proportions of ferric chloride and potassium ferrocyanide and, according to the reaction:

$$FeCl_3 \cdot 6H_2O + K_4[Fe(CN)_6] \cdot 3H_2O \longrightarrow$$

$$\longrightarrow K\,Fe[Fe(CN)_6] \cdot xH_2O + 3\,KCl$$

This substance is known to have the approximate composition K Fe $[Fe(CN)_6] \cdot H_2O$ though the water content is variable (Sharpe 1976).

The product of the reaction was separated in a centrifuge and then washed first with water and alcohol containing a little potassium chloride to avoid peptisation, and after with pure alcohol and ether. It was dried under vacuum at room temperature (Fenger et al. 1970).

3.3-2 Labelling

Soluble Prussian blue was labelled in the cationic site with ^{59}Fe, supplied by the Amersham Centre as ferric chloride in 0.1 M HCl.

A calculated portion of the active solution was added to an inactive ferric chloride solution which was then mixed with potassium ferrocyanide in a 1:1 molar proportion. The precipitate was then separated in a centrifuge and washed according to the procedure described in section 3.3-1.

The specific activity of $K^{59}Fe[Fe(CN)_6].xH_2O$ was 0.01 µCi/mg.

3.3-3 Analysis

The carbon and nitrogen contents were determined by micro-analysis.

The extent of hydration was determined by the loss of weight of a sample heated in an air oven at 100°C.

The results found agree with the composition $K Fe[Fe(CN)_6].3H_2O$:

		found (%)	calcd. (%)
C	-	19.73	19.96
N	-	23.12	23.28
H_2O	-	15.01	14.97

3.4 $[Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3.H_2O$ - hexaaquoiron (III) - aquoethylenediaminetetraacetatoferrate (III) monohydrated

3.4-1 Preparation

Preparation of iron (III)-aquoethylenediaminetetraacetatoferrate (III) has usually proceeded via the complex acid $H[Fe\ EDTA\ (H_2O)]$, hydrogen aquoethylenediaminetetraacetatoferrate (III).

Lambert *et al.* (1963) prepared the complex acid by treating iron (III) hydroxide with a slight excess over the stoichiometric amount of ethylenediaminetetraacetic acid (H_4EDTA). The mixture was heated, with constant stirring, for approximately one hour until no residue remained. Uncomplexed free acid that precipitated when the solution cooled to room temperature was filtered from the solution. Bright yellow crystals of H[Fe EDTA(H_2O)] were obtained after evaporation and the addition of acetone. Lambert and collaborators (1963) found that when an excess of iron (III) hydroxide was used to prepare the complex acid, a brownish compound was obtained.

Analysis of the brownish compound gave the following values for carbon, hydrogen, nitrogen and iron: C - 28.08%; H - 4.28%; N - 6.47%; and Fe - 18.92%, indicating a ratio of Fe : EDTA : H_2O of 4:3:10. The theoretical values for $C_{30}H_{56}Fe_4N_6O_{34}$ are: C - 28.41%; H - 4.45%; N - 6.63% and Fe - 17.61%.

Kennard (1967) prepared the complex acid by refluxing equimolar quantities of a slurry of freshly-precipitated iron (III) hydroxide with an aqueous suspension of H_4EDTA. Further evaporation of the original reaction solution yielded amber crystals. Analysis of the product obtained gave C - 28.45%; H - 4.42%; N - 6.71% and Fe - 18.46%. The formula was written as $[Fe(H_2O)_6]$ $[Fe\ EDTA\ (H_2O)]_3 . H_2O$, since no infrared peak assigned to an uncomplexed carboxilic acid could be found (Morris & Busch 1956).

<u>Preparation</u> The following procedure was adopted for the synthesis of this compound since it did not need high temperatures and allowed easy radioactive labelling.

A solution of the complex acid H[Fe EDTA(H_2O)], prepared according to the method of Lambert *et al.* (1963) described above, was used to saturate a column of anionic resin, Amberlite IRA-401 (Cl) in the form R-[Fe EDTA (H_2O)]$^-$. The product Na[Fe EDTA (H_2O)] supplied by BDH was also employed for this purpose.

The resin was carefully washed with water and then a concentrated solution of ferric nitrate was percolated through it, the following reaction taking place:

$$Fe\ (NO_3)_3 + 3R - [Fe\ EDTA(H_2O)]^- \rightleftharpoons$$

$$\rightleftharpoons [Fe\,(H_2O)_6][Fe\ EDTA\ (H_2O)]_3 + 3R - NO_3^-$$

The eluate yielded amber crystals after complete evaporation in a freeze-drying system. This procedure worked especially well with the labelled material, since exchange in solution between the two iron species is not favoured under these conditions.

The ion-exchange tube was 27 cm long and 2 cm in internal diameter and it contained 70 ml of wet resin. The exchange capacity of the wet resin is 1.25 meq/ml (BDH 1977). Three grams of ferric nitrate (nonahydrated), dissolved in the minimum quantity of water, were employed in the preparation.

The ion-exchange column, the flasks containing solutions of $[Fe\ EDTA\ (H_2O)]^-$, and the flasks containing the final product, were wrapped in aluminium foil to protect them from sunlight. This was necessary since the complex $[Fe\ EDTA\ (H_2O)]^-$ undergoes a light-induced reduction (Jones & Long, 1952, Lambert et al. 1963).

3.4-2 Labelling

The labelled compound was prepared using the procedure described in section 3.4-1, with the difference that $^{59}Fe(III)$, supplied as ferric chloride in 0.1 M HCl solution, was added to the eluant to give $[^{59}Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3 \cdot xH_2O$. The specific activity of the labelled compound was 0.03 µCi/mg.

3.4-3 Analysis

The content of iron was determined volumetrically with potassium dichromate, according to the standard analytical procedure (Vogel 1961), after decomposition of the complex with concentrated sulphuric acid. Iron (III) was reduced to iron (II) with stannous chloride solution.

Analysis of carbon, hydrogen and nitrogen contents were carried out by the microanalysis group of the Chemistry Department, University of Cambridge. The results are shown below, together with the theoretical values for $[Fe(H_2O)_6][Fe\ EDTA(H_2O)]_3 \cdot H_2O$:

		found (%)	calcd. (%)
Fe	-	17.80 ± 0.35	17.62
C	-	28.47	28.41
H	-	4.32	4.45
N	-	6.81	6.63

The infra-red spectra obtained by the potassium bromide disc method did not show peaks at 1200 and 1758 cm^{-1} assigned to an uncomplexed carboxilic acid (Kennard 1967).

3.5 $[Co\ (NH_3)_5\ Cl]\ Cl_2$ - chloropentamminecobalt (III) chloride

3.5-1 Preparation

Chloropentamminecobalt (III) chloride has been prepared in many different ways. Yörgensen (1898) began with chlorotetramminecobalt (III) chloride to obtain the aquo-salt $[CO\ (NH_3)_5H_2O]$

$.Cl_3$. He then treated this with concentrated hydrochloric acid to precipitate $[Co\ (NH_3)_5Cl]Cl_2$.

Biltz (1928) reported a method that began with cobalt (II) chloride and involved preparation of a carbonatotetrammine salt by oxidation in air followed by reaction with ammonia and hydrochloric acid.

Willard and Hall (1922) developed a procedure using the reaction of hydrogen peroxide with hexamminecobalt (II) chloride in the presence of ammonium chloride. This method was later modified by Schlessinger (1967).

Chloropentamminecobalt (III) chloride has also been produced by treating $[Co\ (NH_3)_4(H_2O)_2]\ (NO_3)_3$, $[Co\ (NH_3)_4\ Cl_2]\ NO_3$, or $[Co\ (NH_3)_4\ (H_2O)\ Cl]\ (NO_3)_2$ with excess aqueous ammonia followed by hot hydrochloric acid (Schlessinger 1960).

Other methods have proceeded via cobalt (III) complexes such as $[Co\ (NH_3)_5NO_2]\ (NO_3)_2$, $[Co\ (NH_3)_5\ CO_3]\ NO_3$, or $[Co\ (NH_3)_5\ H_2O](NO_3)_3$; these were heated with concentrated hydrochloric acid to precipitate $[Co\ (NH_3)_5\ Cl]\ Cl_2$ (Basolo & Murmann 1953).

<u>Preparation</u> Chloropentamminecobalt (III) chloride was obtained from the Part II Laboratory of the Chemical Laboratories, University of Cambridge. It was prepared via the following gross reaction:

$$Co\ (H_2O)_6^{2+} + \xrightarrow[O_2]{(NH_4)_2\ CO_3 \cdot NH_3} [Co\ (NH_3)_5\ CO_3]\ NO_3 +$$

$$+ \xrightarrow{HCl} [Co\ (NH_3)_5Cl]\ Cl_2$$

The method began with the preparation of $[Co(NH_3)_5CO_3]NO_3$ by mixing a solution of cobalt (II) nitrate with a solution of ammonium carbonate and concentrated ammonia. A stream of air was bubbled through the mixture for 24 hours and the resulting solution cooled in an ice-bath. The product, $[Co(NH_3)_5CO_3]NO_3$, was collected as crystals and washed with a little ice-cold water, followed by alcohol and ether. The pure crystals were then dissolved in water at 80-90°C, and 5N hydrochloric acid added until evolution of carbon dioxide was almost complete. Following this, concentrated hydrochloric acid was added, the solution kept at 80°C for about 10 minutes, and then cooled in an ice-salt bath. Crystals of $[Co\ (NH_3)_5\ Cl]\ Cl_2$ separated out and these were filtered, washed with alcohol and ether and dried in a vacuum desiccator at room temperature.

3.5-2 Labelling

Chloropentammine cobalt (III) chloride was labelled both in the cationic and anionic sites. The radioisotope ^{36}Cl, supplied by the Amersham Centre as a 0.1-0.3 M HCl solution, was used. It had an activity of 100 μCi in a total volume of 1.1 ml and containing 7 mg Cl/ml.

(i) The compound was labelled in the anionic site according to the following procedure:

An aliquot of 0.3 ml of the radioactive solution, containing 27.3 μCi of ^{36}Cl, was diluted to 100 ml and percolated through a column of anionic resin in the form $R\text{-}Cl^-$. Amberlite IRA-400 (Cl) was used in a column 15 cm long and 1 cm internal diameter. ^{36}Cl was removed from the solution by an isotopic exchange reaction:

$$R\text{-}\overset{*}{Cl}^- + H^{36}Cl \rightleftharpoons R\text{-}{}^{36}Cl^- + HCl$$

After this, a solution of $[Co\ (NH_3)_5\ Cl]\ Cl_2$ (2.5 g dissolved in 650 ml water), was percolated through the labelled resin and ^{36}Cl introduced into the inactive compound by the exchange reaction:

$$2R\_\ {}^{36}Cl^- + [Co\ (NH_3)_5\ Cl]\ Cl_2 \rightleftharpoons 2R\_\ Cl^- + [Co\ (NH_3)_5\ Cl]^{36}Cl_2$$

This method of labelling was suggested by the work of Peters and Fiore (1974), who employed the isotopic ion-exchange technique to remove traces of a radioactive element from a solution by passing it through a column of resin previously saturated with the same stable ion.

The eluate was divided between four 500 ml round flasks and the solution inside was frozen forming a thin layer around the flask walls. The flasks were then attached to a freeze-drying system.

The solid compound $[Co\ (NH_3)\ Cl]^{36}\ Cl_2$ was obtained either by completely freeze-drying the solution or by precipitation of the compound from the cooled solution following partial freeze-drying. The two preparations so obtained will be referred to as samples A and B, respectively.

(ii) Chlorine-36 was introduced into the complex $[Co\ (NH_3)_5\ Cl]^{2+}$ using the method reported by Laurie and Monk (1965) as follows:

About 3 g of aquopentamminecobalt (III) chloride, $[Co\ (NH_3)_5\ H_2O]Cl_3$, were dissolved in a minimum volume of water at 80°C. Twenty µCi of ^{36}Cl were added and the temperature kept stable for 4 hours. The chlorosalt was precipitated by the addition of 100 ml of concentrated hydrochloric acid.

Any chlorine-36 outside the complex ion was removed by dissolving the active crystals in a minimum volume of water at 35°C followed by reprecipitation after the addition of a large excess of concentrated hydrochloric acid.

The starting-point for the preparation of the aquopentamminecobalt (III) chloride salt was aquopentamminecobalt (III) perchlorate $[Co(NH_3)_5H_2O](ClO_4)_3$. The perchlorate was dissolved in a little water and N-hydrochloric acid added. $[Co(NH_3)_5H_2O]Cl_3$ was precipitated by cooling in an ice-bath with the addition of concentrated hydrochloric acid. The crystals were filtered and freed from perchlorate by washing with hydrochloric acid diluted with water in the ratio 1:1. Excess acid was removed by washing with alcohol (Yörgensen 1898).

The perchlorate salt was prepared by acidifying carbonatopentamminecobalt (III) nitrate with 2M-perchloric acid and heating the solution to boiling. The perchlorate salt crystallized on cooling. The product was purified by recrystallisation from dilute perchloric acid and from water (Rutenberg & Taube 1952). $[Co(NH_3)_5CO_3]NO_3$ was obtained from the Part II Laboratory of the Chemical Laboratories, University of Cambridge.

3.5-3 Analysis

A sample of chloropentamminecobalt (III) chloride was analysed for hydrogen, nitrogen and chlorine by the microanalysis group of the Chemical Laboratories. The results are shown below, together with the theoretical values for $[Co(NH_3)_5Cl]Cl_2$:

		found (%)	calcd. (%)
H	-	5.95	6.04
N	-	28.10	27.96
Cl	-	42.11	42.47

3.6 $Cr_2\ (C_2O_4)_3.6H_2O$ - chromium (III) oxalate hexahydrated

3.6-1 Preparation

Methods of preparation of $Cr_2\ (C_2O_4)_3\ .\ x\ H_2O$ from the reaction of $K_2Cr_2O_7$, K_2CrO_4 or CrO_3 with oxalic acid have been reported (Bothamley 1887, Werner 1888, Lapraik 1893). Different hydrates of chromium (III) oxalate have also been synthesised (Gmelins 1962).

Douvillé *et al.* (1942) reported they had prepared the compound $[Cr\ (H_2O)_4][Cr\ (C_2O_4)_3]$ by passing a hot solution of oxalic acid several times through a bed of freshly-precipitated chromic hydroxide.

Kawamura and Wada (1957) synthesised the compound $[Cr(H_2O)_6]$ $[Cr(C_2O_4)_3]$ by passing potassium trioxalatochromiate through a column of cationic resin to remove potassium, and reacting the product with hexaaquochromium sulphate in the presence of barium hydroxide to precipitate the sulphate ions. The product was unstable in solution since oxalate ions migrated to the cationic side, giving the compound $[Cr\ (C_2O_4)(H_2O)_4].[Cr\ (C_2O_4)_2(H_2O)_2]$, a stable product.

Preparation a) A fast method for the preparation of the compound $[Cr\ (H_2O)_6][Cr\ (C_2O_4)_3]$ was used to avoid decomposition while in solution. The method also allowed the labelling of the compound in only one site; it was based on the following reactions:

$$3R\_Cl^- + K_3[Cr(C_2O_4)_3].3H_2O \rightleftharpoons R_3\text{-}[Cr(C_2O_4)_3]^{3-} + 3KCl$$

$$R_3\text{-}[Cr(C_2O_4)_3]^{3-} + Cr(ClO_4)_3.6H_2O \rightleftharpoons 3R\text{-}ClO_4^- + [Cr(H_2O)_6][Cr(C_2O_4)_3]$$

Potassium trioxalatochromiate was percolated through a column of anionic resin, Amberlite IRA-401 (Cl) until complete saturation in the form $R_3\text{-}[Cr(C_2O_4)_3]^{3-}$ had occurred.

The resin was carefully washed and a concentrate solution of chromium perchlorate was percolated through it, forming $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ in the eluate. The solution was frozen immediately and then freeze-dried, forming very fine blue crystals.

The ion-exchange tube was 27 cm long and of 2 cm internal diameter, containing 70 ml of wet resin (exchange capacity: 1.25 meq/ml). Around 3.5 g of chromium perchlorate dissolved in the minimum quantity of water, were employed in the preparation.

Potassium trioxalatochromiate was prepared according to the reaction (Booth 1939):

$$K_2Cr_2O_7 + 7H_2C_2O_4 + 2K_2C_2O_4 \longrightarrow 2K_3[Cr(C_2O_4)_3].3H_2O + 6CO_2 + H_2O$$

Potassium dichromate was added slowly, and with constant stirring, to a mixture of potassium oxalate monohydrate and oxalic acid dissolved in water. When the reaction had ceased, the solution was evaporated nearly to dryness and allowed to crystallise.

b) The method of Douvillé <u>et al</u>. (1942) was employed in trying to obtain the compound $[Cr(H_2O)_4][Cr(C_2O_4)_3]$ by reacting a hot solution of oxalic acid with freshly-precipitated chromic hydroxide. The resultant solution was evaporated to give a product of syrupy consistency. The evaporation of the remaining solution was completed at room temperature under vacuum, or by freeze-drying, when violet-green crystals of indefinite shape were formed; this product was found to be $[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$.

3.6-2 Labelling

a) $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ was labelled in the cationic side with ^{51}Cr, received from the Amersham Centre as $Na_2{}^{51}CrO_4$ in aqueous solution with a total activity of 10 mCi in 2.1 ml and containing 24 µg Cr/ml.

The volume of the radioactive solution was made up to 20 ml and chromium (VI) was reduced to chromium (III) by the addition of 3 ml of concentrated hydrochloric acid and alcohol, boiling the solution until it was colourless and no longer smelled of alcohol.

Two mCi of ^{51}Cr (III) were then added to a solution of chromium perchlorate, used to obtain the labelled compound $[^{51}Cr(H_2O)_6][Cr(C_2O_4)_3]$, by the procedure described in section 3.6-1, a). The labelled compound was stored in a dewar flask containing solid CO_2.

b) The compound $[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$ was labelled in the cationic side with $^{51}Cr(III)$, according to the following procedure:

A dilute solution containing 10 mCi of $^{51}Cr(III)$ was percolated through a column of cationic resin (Amberlite IR-120 (H)) containing 10 ml of the wet resin saturated in the R_3-Cr^{3+} form. $^{51}Cr(III)$ was fixed in the resin by the isotopic exchange reaction:

$$R_3 - Cr^{3+} + {}^{51}Cr^{3+} \rightleftharpoons R_{3}- {}^{51}Cr^{3+} + Cr^{3+}$$

Then a solution of the inactive compound was put in contact with the labelled resin for one hour. Hence, $^{51}Cr(III)$ was introduced by another exchange reaction:

$$R_3 - {}^{51}Cr^{3+} + [Cr(C_2O_4)(H_2O)_4]^+ \rightleftharpoons$$

$$\rightleftharpoons R_3 - Cr^{3+} + [{}^{51}Cr(C_2O_4)(H_2O)_4]^+$$

This reaction was not very effective as it gave a product with low specific activity. Furthermore there was the possibility of cation exchange between Cr^{3+} from the resin with $[Cr(C_2O_4)(H_2O)_4]^+$ although the error due to this reaction was negligible because of the greater affinity of the resin for Cr^{3+} than for $[Cr(C_2O_4)(H_2O)_4]^+$.

The solid compound obtained after freeze-drying the labelled solution was stored in a dewar flask containing solid CO_2.

3.6-3 Analysis

The content of chromium in both compounds was determined by titration with standard ferrous solution, after oxidation to dichromate by boiling with excess ammonium persulphate in the presence of silver nitrate as catalyst (Vogel 1961).

The carbon and hydrogen contents were determined by microanalysis. The results for $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ and

$[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$ were, respectively:

			found (%)	calcd.(%)
$[Cr(H_2O)_6][Cr(C_2O_4)_3]$				
	C	-	15.32	15.13
	H	-	2.64	2.54
	Cr	-	21.83 ± 0.27	21.84
$[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$				
	C	-	14.97	15.13
	H	-	2.57	2.54
	Cr	-	21.66 ± 0.36	21.84

Some decomposition of $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ to $[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$ might have occurred. To check this the content of oxalate was determined in the anionic fraction of the compound $[Cr(H_2O)_6][Cr(C_2O_4)_3]$. The separation of the two chromium species was done by cation exchange, according to the procedure described in chapter 4, section 4.8-1.

The oxalate content was determined after decomposing the complex with hot potassium hydroxide and filtering the precipitated chromium (III) hydroxide. The filtrate was acidified, treated with excess standard cerium (IV) solution, boiled, and after cooling, back-titrated with standard ferrous solution (Hamm 1953, Vogel 1961). The analysis gave 53.91% of oxalate in the anionic fraction, which when compared with the theoretical value of 55.45%, indicated that a migration of 1.54% of oxalate to the cationic side had occurred, corresponding to a decomposition of 8.33%.

The presence of oxalate in the cationic side of the compound was confirmed when part of the chromium which had been fixed in the resin was eluted with 0.05 N perchloric acid. In such a low concentration, perchloric acid elutes only $[Cr(C_2O_4)(H_2O)_4]^+$ and not $[Cr(H_2O)_6]^{3+}$ (Kawamura & Wada 1957).

The oxalate content was also determined in the anionic side of the second compound $[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$ by the same procedure. The result was 37.03 ± 0.7%, corresponding to 2/3 of the total oxalate in the compound. The theoretical values are 36.97% for oxalate in the anionic side, and 55.45% for total oxalate in the compound.

3.7 Treatments of the labelled compounds

Samples of the labelled compounds were treated in different ways, as described below, in order to induce exchange between the isotopic species in the compounds and to observe the influence of defects on the mechanisms of these reactions.

3.7-1 Thermal treatment

Thermal treatment was carried out in a thermostatically-controlled oven. Each sample was placed in a glass ampoule and sealed under atmospheric pressure. Each was heated for different times and at different temperatures, the length of time and range of temperature varying with the compound.

3.7-2 Gamma irradiation

Samples of the different labelled compounds were sealed in glass ampoules under atmospheric pressure and irradiated in the Co-60 gamma source of the Chemical Laboratories at room temperature. The source intensity was 7.2 x 10^4 rads per hour, but the total dose absorbed varied from compound to compound.

3.7-3 Crushing

Crystals of the untreated labelled compounds were crushed in an agate mortar into very fine powder.

3.8 Counting of activity

A Geiger-liquid counting tube (10 ml) was used for counting the radioactivity. By adding an adaptor with a quench unit and a scaler, the apparatus provided a single-channel G-M counter system. A power-unit connected to the mains supplied low DC voltage to the adaptor. The high voltage was periodically checked and adjusted so that the counter was operating on the plateau of the counting-rate/voltage characteristic.

Aliquots of 10 ml of the radioactive solutions were always used for counting. Corrections were made for the background count, but generally no corrections for decay were necessary because, in most cases measurements were made with a short time interval between the countings. Corrections for decay were necessary only for the chromium oxalates.

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CHAPTER 4 - THE SELECTION OF SYSTEMS FOR STUDY

An exchange reaction between two normal lattice entities in a solid compound is usually studied in the following manner:

(i) an isotopic label is introduced into one of the sites of the compound;

(ii) the exchange is then allowed to occur or is induced by heating or other means;

(iii) next the two exchanging species are separated;

(iv) finally the distribution of radioactivity at the end of the operation is measured.

The transfer of radioactivity is generally followed by measuring the fraction of exchange either as a function of time at a constant temperature, or as a function of temperature for a constant period of time. The kinetic parameters of the reaction can be obtained from these isothermal and isochronal curves.

The shapes of the experimental curves also contain information about the processes being studied. Isochronal curves are more informative in this respect. They may show either a steady change with temperature or sloping regions followed by flat or nearly flat regions. This may indicate that different exchange processes become active at successively higher temperatures. A sloping region of the curve shows that the rate of one or more processes may be changing. In the subsequent flat region, no further processes have yet become active or the processes may be so fast that they are complete during the exchange period. It is often possible to determine the number of processes involved from an isochronal curve showing these characteristics. Further, the relative activation energies can be found from such a curve since the temperatures at which each reaction becomes active is well-determined.

Isothermal curves are not so informative although information about the kinetic parameters of the reaction can be obtained.

The influence of defects on the processes under investigation can be observed if samples of the labelled compounds are subjected to such treatment as gamma-irradiation or crushing before heating, the shapes of the experimental curves and the kinetic parameters giving us some insight into the mechanisms involved. The influence of other processes such as hydration, dehydration and in some cases, decomposition, can also be informative.

The progress of an exchange reaction in the solid-state can only be followed if the compound under investigation possesses a certain number of characteristics. These characteristics, together with the selection procedures employed to choose suitable compounds for exchange studies are discussed in the next section.

4.1 Selection procedures

Exchange studies between two normal lattice species has to be made in systems in which one kind of atom has been radioactively labelled and, after separation of the two species in the freshly-labelled material, no substantial exchange takes place. The compound must be stable over a certain temperature range and it should be possible to induce exchange by one or more of the different treatments such as heating, gamma-irradiation, crushing of the crystals, etc.

The selected compounds were synthesised, labelled and analysed as described in chapter 3. The choice was influenced by several factors including the interest in studying systems as yet unexplored, and the possibilities offered by different compounds of investigating various aspects of the exchange process, such as the exchange between atoms having the same or different oxidation states or between ligand atoms and isotopic atoms outside the coordination sphere. Other factors taken into account include the nuclear properties of the radioisotope that would be used for labelling, and, when available, data about the thermal stability of the compound, the exchange in solution of the species under consideration, and such other information as would indicate the suitability of the system for solid-state exchange studies.

A practical selection procedure was adopted by which those compounds suitable for exchange investigations could be selected. It was as follows:

(i) The extent of exchange induced by the synthesis-separation process was measured before further treating the sample. If the fraction of exchange was less than about 10% (in most cases), the compound was retained for the subsequent tests.

(ii) An attempt was made to induce exchange by heating or by other treatment. Those compounds in which it was not possible to induce exchange were discarded.

(iii) A check was made to ensure that the treatment given to the sample did not cause decomposition as well as exchange.

If the process of exchange could not be distinguished from that of decomposition, the compound was not considered suitable. If there was no considerable decomposition the compound was then selected for further investigation.

The application of this selection procedure is presented in sections 4.3 - 4.8, under the title of each compound investigated. In the next section the fraction of exchange is defined, together with the correction applied to account for activity inherent in the species that was initially inactive before treatment. Some other systems were discarded on the basis of the above tests.

4.2 The fraction of exchange and correction for an apparent zero-time exchange

The fraction of exchange at time t in an homogeneous exchange reaction between reactants A and B, both containing a given element X that exchanges under a specified set of conditions, and where B only is initially labelled, may be expressed as (see Appendix 1)

$$F = \frac{S_A}{S_{A_\infty}} \tag{4.1}$$

where A is the species initially inactive, and S_A and S_{A_∞} are the specific activities of A at time t and at equilibrium respectively.

We define the specific activity as the ratio of radioactive X atoms to the total number of X atoms (active plus inactive) in reactant A. Expression (4.1) then becomes

$$F = \frac{x}{x_\infty} \tag{4.2}$$

where x and x_∞ are the numbers of active X atoms contained in species A at time t and at equilibrium respectively. This may also be written as

$$F = \frac{a}{a_\infty} \qquad (4.3)$$

where a and a_∞ are the activities proportional to x and x_∞ respectively.

The fraction of exchange, F', observed at time t after the separation of species A and B, is equal to F when the separation of the two species is complete and no exchange occurs during separation. However, when the separation of the reactants is incomplete or when the separation process itself induces exchange, these effects result in an "apparent zero-time exchange". The synthesis of the compound itself can also cause this effect.

Prestwood and Wahl (1949) demonstrated that the following correction may be made for an incomplete, apparent, zero-time exchange if the separation-induced exchange and the incomplete-separation effects are reproducible (see Appendix 2 for the derivation):

$$F = \frac{S - S_0}{S_\infty - S_0} = \frac{F' - F'_0}{1 - F'_0} \qquad (4.4)$$

where S and S_0 are the specific activities of the chemical fraction enriched in A and separated from the reaction mixture at time t and time zero, respectively. S_∞ is the equilibrium specific activity of A. F' and F'_0 are the fractions of exchange observed after separation at times t and time zero, respectively, and expressed as

$$F' = \frac{S}{S_\infty} \qquad (4.5)$$

and $$F'_o = \frac{S_o}{S_\infty} \quad . \tag{4.6}$$

Equation (4.4) includes the correction for synthesis-induced exchange, because the fraction of X atoms initially in B, that end up in A after the synthesis of the compound, are included in the measurement of S_o.

The distinction between incomplete separation and separation and/or synthesis-induced exchange can only be made on the basis of further evidence, such as may be provided, for example, by the presence of B in a precipitate of A.

The fraction of exchange obtained from the experimental data was expressed as a percentage as follows:

$$E(E'_o, E') = F(F'_o ; F') \text{ X } 100\%.$$

4.3 Hg[Hg EDTA]. x H_2O - mercury (II) - ethylenediaminetetra-acetatomercurate (II) hydrated

The double mercury salt, Hg[Hg EDTA] x H_2O, was chosen as it allowed the study of the exchange between two isotopic species lying in two different coordination sites and having the same oxidation state, a situation that has been explored only once before (Nyarku 1978). Besides this, the radioactive isotope ^{203}Hg has advantageous nuclear properties (Lederer *et al*. 1967):

Radioactive isotope	Half-life	Major radiations approximate energies (MeV) and intensities	
^{203}Hg	46.9 d	β^-	0.214 max
		e^-	0.194, 0.264, 0.275
		γ	0.279 (77%)

Furthermore, the complex $[Hg\,EDTA]^{2-}$ has a high stability constant diminishing the likelihood of exchange in solution (K_1 = 21.8) (Anderegg 1964).

4.3-1 Separation procedures

To separate the species Hg^{2+} from $[Hg\,EDTA]^{2-}$ in the compound $^{203}Hg\,[Hg\,EDTA].2H_2O$, the cationic mercury was precipitated by the addition of 2 ml 1M-sodium hydroxide to a suspension of ca. 20 mg of the compound in 2 ml of water. The precipitate was separated by centrifugation, washed twice with water, and all the supernatant liquids were combined and counted as complex mercury. The precipitate was dissolved with 6N-nitric acid and counted as the cationic mercury fraction.

The mercury content of the cationic fraction was determined volumetrically with thiocyanate to check the selectivity of this method of separation (Hillebrand et al. 1953). 99.5 ± 0.6% of the cationic mercury was measured in the precipitated fraction and the separation was considered complete within the experimental error.

4.3-2 Selection tests

(i) Zero-time exchange

The fraction of exchange measured after the separation of Hg^{2+} and $[Hg\,EDTA]^{2-}$ and before any treatment was given to the sample was:

$$E'_0 = 100 \pm 2\%$$

4.3-3 Conclusion

The exchange between the two mercury species in the compound $^{203}Hg[Hg\,EDTA].2H_2O$ goes to completion during the synthesis-separation processes; therefore no other experiment was done with it. It was not possible to discover whether the exchange occurred during the synthesis or during the separation of the compound, or both. As no other method of synthesis or separation was available this compound was discarded.

4.4 Fe [Fe $(CN)_5NO$]. x H_2O - iron (II) - pentacyanonitrosylferrate (III) hydrated

The compound Fe [Fe $(CN)_5NO$]. x H_2O was chosen because in this system the progress of the exchange between the two iron species in the cationic and anionic sites might be followed not only by chemical analysis but also in situ by Mössbauer spectroscopy using labelling with ^{57}Fe.

The nuclear properties of the radioisotope ^{59}Fe are also favourable for exchange studies (Lederer et al. 1967):

Radioactive isotope	Half-life	Major radiations approximate energies (MeV) and intensities
^{59}Fe	45.6 d	β^- 1.57 max (0.3%), 0.475 max γ 0.143 (0.8%), 0.192 (2.8%) 1.095 (56%) 1.292 (44%)

The chemical and physical properties of the nitroprusside ion (pentacyanonitrosylferrate (III)) have been reviewed by Swinehart (1967), where the controversy about the oxidation state of the iron in $(NC)_5FeNO^{2-}$ was discussed.

Sharpe (1976) concludes from his study of the chemistry of cyano complexes of the transition metals that there is no nitrosopentacyano complex of iron (III). Therefore, the formula of the compound is better written as Fe (II) $[Fe(II)(CN)_5NO].xH_2O$.

4.4-1 Separation procedures

The procedure of Cambi and Clerici (1928) was used to separate Fe^{2+} from the complex $[Fe(CN)_5NO]^{2-}$. The oxide of iron was precipitated at low temperature with 2N-potassium hydroxide (2 ml) in a sample of the compound (ca. 40 mg) suspended in water (1 ml), and the precipitate separated by centrifugation and washed twice with water. The supernatant liquids contained regenerated nitroprussiate; they were combined and counted as complex iron. The activity that remained in the cationic fraction was also counted when the precipitate had been dissolved in hydrochloric acid.

It was necessary to check whether this procedure led to a complete separation of the two iron species; the iron content of the cationic fraction was therefore determined volumetrically with potassium dichromate (Vogel 1961). It was found that 100.5 ± 0.7% of the iron in the cationic fraction was precipitated, indicating (within the experimental error) a complete separation of the exchanging species.

4.4-2 Selection tests

(i) Zero-time exchange

The distribution of radioactivity between Fe^{2+} and $[Fe(CN)_5NO]^{2-}$ was measured in a sample of the compound labelled initially in the cationic side, after the separation of the two species and before any further treatment.

The percentage of exchange found was:

$$E_o' = 1.8 \pm 0.2\%$$

This result was low enough to warrant further investigation of this compound.

(ii) Sample treatments

a) Thermal treatment. Samples of approximately 40 mg of the radioactive compound were sealed in glass ampoules and heated in an air oven for 16 hours at temperatures between 33°C and 130°C. The fraction of exchange was then measured, with the results shown in Table 4.1 and presented graphically in Figure 4.1. Values have been corrected for the zero-time exchange.

The experimental results show that exchange is barely enhanced by increasing the temperature until 120-130°C when decomposition begins.

b) Gamma irradiation. Irradiation with gamma rays might cause exchange between the iron species, or it might promote exchange on subsequent heating. To test this a bulk sample of the labelled compound, contained in a sealed glass ampoule, was irradiated at room temperature with gamma rays to a total dose of 7.8 Mrads. The exchange percentage measured after the irradiation and before heating was 1.9 ± 0.2%, showing that the radiation by itself did not induce exchange.

Samples of the irradiated material were then sealed in glass ampoules and heated in an air oven for 16 hours at temperatures between 33°C and 155°C. The fractions of exchange were measured and corrected for zero-time exchange; the results are shown in Table 4.1 and represented graphically in Figure 4.1

Table 4.1 Isochronal heating of $^{59}Fe[Fe(CN)_5NO].5H_2O$

Time: 16 hours

Sample	Temperature T (^oC)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
Untreated sample	33	0.3	99.7
	60	0.2	99.8
	100	0.6	99.4
	120	1.5	98.5
	130	2.3	97.7
Gamma-irradiated sample	20	0.1	99.9
	33	0.3	99.7
	100	0.7	99.3
	125	2.1	97.9
	130	2.5	97.5
	155	23.8	76.2

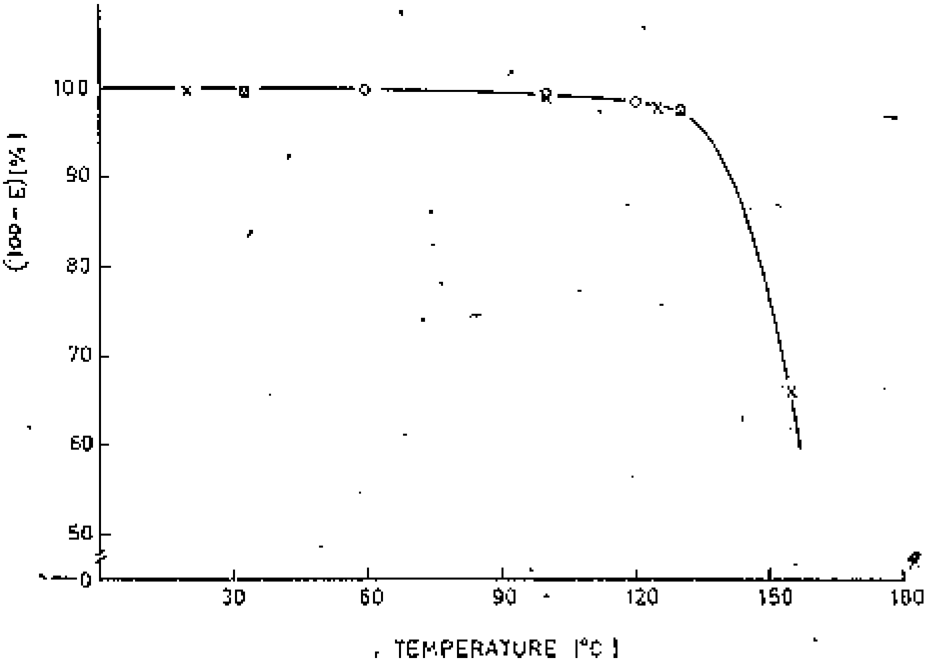

Fig. 4.1 The exchange isochronal of $^{59}Fe[Fe(CN)_5NO].xH_2O$.

Time: 16 hours.

O : untreated sample

X : γ-irradiated sample (7.8 Mrad).

together with the values obtained for the untreated sample. They show that the irradiation did not promote subsequent thermal exchange. Again exchange was only observed when decomposition set in.

(iii) Crushing. A portion of the untreated labelled compound was crushed in an agate mortar and a sample was heated at 90°C for 16 hours. The exchange percentages measured before and after heating showed that exchange is neither promoted by crushing nor does it facilitate subsequent thermal exchange.

It is very likely that crushing failed to induce exchange because the untreated compound was already powdery in nature.

4.4-3 Conclusion

Since exchange could not be observed without decomposition, no further experiments were performed with the compound $Fe[Fe(CN)_5NO] \cdot xH_2O$.

4.5 $K Fe [Fe(CN)_6] \cdot xH_2O$ - soluble Prussian Blue

Exchange between the two iron species in soluble Prussian Blue has already been explored to some extent (Thompson 1948). It appears that there is no isotopic exchange between the two iron species in this compound, either in colloidal dispersion or in the solid state. Fenger and Maddock (1970) found no exchange induced by heating or gamma radiation in samples heated to 100°C or dosed with 10 Mrads of ^{60}Co-radiation.

In the present study we investigate whether crushing can promote exchange.

4.5-1 Separation procedures

We used the method of Fenger et al. (1970) to separate the cationic and anionic iron species. It consisted in the precipitation of ferric hydroxide by the addition of 1M -sodium hydroxide (5 ml) to a sample of the compound (25 mg) suspended in water (3 ml). Ferric hydroxide was precipitated and was coagulated by warming and separated from the supernatant by centrifugation. It was washed twice with a 1% sodium chloride solution made alkaline with a little sodium hydroxide. The precipitate was then dissolved in hydrochloric acid and the solution was counted as the cationic iron fraction. The supernatant liquid, combined together, were counted as the complex-iron fraction.

The separation procedure was tested by determining the proportion of iron in the cationic fraction volumetrically with potassium dichromate after reduction of iron (III) to iron (II) with stannous chloride solution (Vogel 1961).

100.5 ± 0.2% of the cationic iron was precipitated this way suggesting that the separation of the two iron species was complete within the experimental error.

4.5-2 Selection tests

(i) Zero-time exchange

The exchange percentage was measured in a sample of soluble Prussian Blue labelled in the cationic side, after the synthesis-separation procedures and before any treatment was given to the sample; the result was

$$E_0^1 = 1.1 \pm 0.1\%$$

showing, as expected, that practically no exchange takes place during the synthesis-decomposition processes.

(ii) Sample treatments

a) Crushing. A portion of the labelled compound was crushed in a mortar to a very fine powder and a sample was sealed in a glass ampoule and heated at 90°C for 16 hours. The exchange percentage measured after this treatment, and corrected for zero-time exchange, was 0.02%, showing that crushing failed to promote exchange. Again, it is quite likely that this is due to the fact that the untreated substance was already in the form of very fine crystals so that crushing did not induce much of a change.

Heating to higher temperatures, above 100°C, leads to decomposition with no possibility of analysis.

4.5–5 Conclusion

Since it was not possible to induce exchange with the sample treatments employed, no other experiments were performed with soluble Prussian Blue.

4.6 $[Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3 \cdot H_2O$ – hexaaquoiron (III) – aquoethylenediaminetetraacetatoferrate (III) monohydrated

The exchange process in the system iron (III) – aquoethylenediaminetetraacetatoferrate (III) was investigated, both because of the favourable nuclear properties of the isotope ^{59}Fe and because exchange of iron between the aquoferric and ferric ethylenediaminetetraacetate ions in solution was very slow (Jones & Long 1952), so that chemical procedures of separation could be used. The half-life of the exchange in solution varies from 0.5 to 400 hours at high and low pH, respectively.

The choice of this compound was further supported by the possibility of studying the exchange in situ by Mössbauer spectroscopy after labelling with ^{57}Fe.

The Fe (III) chelate contains sexadentate EDTA with a water molecule coordinated to the metal in a structure "loosely describable as pentagonal bipyramidal" (Hoard et al. 1961a,b). The dissociation constant of the ferric complex is about 10^{-24} (Jones & Long 1952), showing that the complex is very stable. Solutions of the Fe (III) chelate are indefinitely stable in the dark, but on exposure to sunlight a light-induced reduction to Fe (II) chelate occurs (Jones & Long 1952).

4.6-1 Separation procedures

The separation of the cationic iron fraction from the anionic complex in the compound $[Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3 \cdot H_2O$ was achieved by ion-exchange. Samples of approximately 50 mg of the compound, labelled initially in the cationic side, were dissolved in water and made up to 25 ml. An aliquot of 10 ml of this solution was used to determine the total activity of the sample, the other 15 ml being transferred to a 100-ml separatory funnel containing 10 ml of cationic resin, Amberlite IR-120 (H) (exchange capacity of the wet resin: 1.9 meq/ml). The mixture was shaken vigorously until the amber colour of the solution had faded to a light yellow indicating the presence in solution of the complex acid $H[Fe\ EDTA\ (H_2O)]$. The liquid phase was separated, the resin was cautiously washed and all the liquids were combined to count as the complex iron.

As a control, the iron content of the anionic fraction was determined, the fraction first being concentrated to a small volume and heated with concentrated sulphuric acid to destroy the complex. Iron was analysed volumetrically with standard potassium dichromate after reduction of ferric iron to ferrous iron with stannous chloride solution (Vogel 1961). The result indicated that separation was complete: 99.8 ± 0.3% of the iron contained in the complex side of the compound $[Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3.H_2O$ was recovered in the fraction separated from the resin.

4.6-2 Selection tests

(i) Zero-time exchange

The exchange percentages measured after the separation of the anionic and cationic fractions of the compound $[^{59}Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3.H_2O$, and before any further treatment was given to the sample were:

$$E'_{oA} = 14.9 \pm 0.3\%$$

$$\text{and}\quad E'_{oB} = 6.2 \pm 0.9\%$$

where A and B refer to the first and second preparations of the labelled compound, respectively.

The lower zero-time exchange for sample B was probably due to the fact that the radioactive solution collected from the column of resin during the preparation of the compound (chapter 3, sections 3.4-1 and 3.4-2) was immediately frozen and then freeze-dried. The second method of preparation was also faster than the first one.

The zero-time exchange was low enough to allow the investigation of the exchange process in the solid state, so the following treatments were given to the labelled samples to try to induce exchange.

(ii) Sample treatments

a) Thermal treatment. Samples of approximately 50 mg of both preparations of the labelled compound (samples A and B) were sealed in glass ampoules and heated for 2.25 hours, at 120°C. The exchange percentages corrected for zero-time exchange were measured to be 4.3 ± 0.7% and 4.9% for A and B respectively. The percentages of exchange were observed to increase with temperature, so that it was necessary to analyse the thermal stability of the compound in order to find out if the exchange process was being induced by decomposition.

(iii) Decomposition analysis

a) Thermogravimetric analysis. A sample of $[Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3.H_2O$ was examined thermogravimetrically, being heated at 5°C/min in a flux of nitrogen, using a Stanton-Redcroft thermobalance. The compound lost weight from 27°C to 120°C. Its weight was then constant until 140°C when a continuous weight loss began again, as shown in Figure 4.2.

The loss of 0.17 mg, or 9.1% of the sample weight (1.87 mg) observed from 27-120°C corresponds to 6.4 molecules of water. This figure is consistent, within the experimental error, with 7, corresponding to the loss of the six molecules of water of the aquoferric ion $[Fe(H_2O)_6]^{3+}$ plus one molecule of water of hydration. This partially-dehydrated product was stable from 120 to 140°C, beyond which it gradually began to lose the water

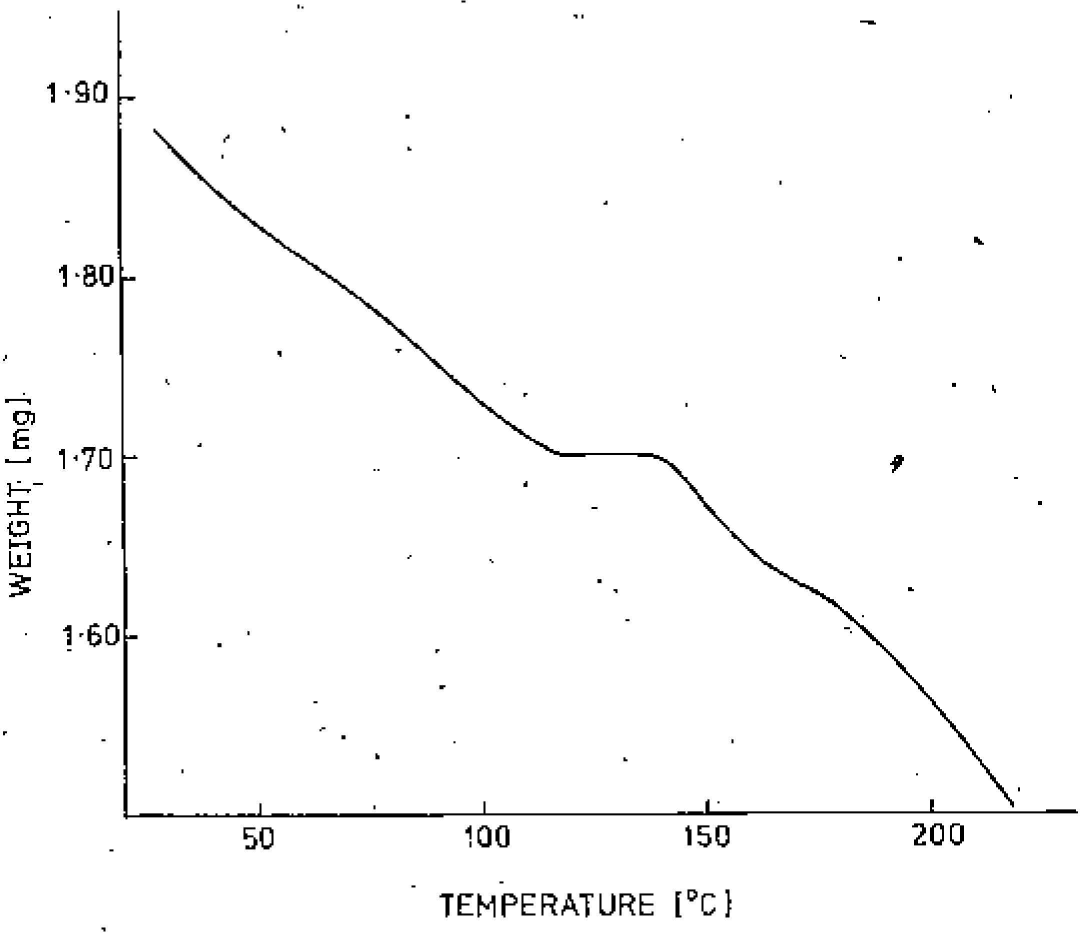

Fig. 4.2 The thermal decomposition curve for $[Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3 \cdot H_2O$.

molecules coordinated to the metal in the complex $[Fe\ EDTA\ (H_2O)]^-$ and to decompose.

b) Spectrophotometric analysis. A spectrophotometric analysis was carried out in order to determine the extent of decomposition of $[Fe\ (H_2O)]$. $[Fe\ EDTA\ (H_2O)]_3.H_2O$ in samples of known weight, each of which had been treated for 2.25 hours in sealed glass ampoules at 120°C, 130°C, 140°C and 150°C. The concentration of the complex in the solutions made with the heated samples was determined by measuring the optical absorption at 256 mμ where $[Fe\ EDTA\ (H_2O)]^-$ has an absorption peak (Reynolds et al. 1961). The absorbance was measured with a Unicam SP600 UV spectrophotometer on the assumption that the molecular extinction coefficients of $[Fe\ EDTA\ (H_2O)]^-$ and $[Fe\ (H_2O)_6]^{3+}$ were 9420 and 3500 $M^{-1}\ cm^{-1}$ respectively.

The percentage of decomposition was normalised to that of an untreated sample of the same concentration. The results showed that there was no decomposition at 120°C, 1.9% at 130°C, 3.1% at 140°C and 26.0% at 150°C.

4.6-3 Conclusion

The exchange observed between the iron atoms in the cationic and anionic sides of the compound $[^{59}Fe\ (H_2O)_6][Fe\ EDTA\ (H_2O)]_3.H_2O$ was found to be induced by thermal treatment at temperatures up to 140°C and not caused by decomposition; this compound was therefore considered suitable for the study of the exchange process in the solid state.

Other treatments, such as gamma-irradiation and crushing, were also given to the samples in order to observe the influence of defects on the exchange process. The results obtained from these experiments are presented in chapter 5.

4.7 $[Co(NH_3)_5Cl]Cl_2$ - chloropentamminecobalt (III) chloride

Previous studies of exchange reactions between normal lattice species in solids have dealt mainly with the central atoms in complex salts. Another interesting situation is presented by the exchange between ligand atoms and atoms outside the coordination sphere. This can be explored using the compound $[Co(NH_3)_5Cl]Cl_2$, which is especially suitable in view of the favourable nuclear characteristics for this kind of study (Lederer et al. 1967) of the radioactive isotope ^{36}Cl:

Radioactive isotope	Half-life	Major radiations approximate energies (MeV) and intensities
^{36}Cl	3.08×10^5 y	β^- 0.714 max y S X-rays 0.511 (0.003%, $\gamma^{\pm}$)

Chloropentamminecobalt (III) chloride forms red-violet rhomb-shaped crystals which decompose on heating with a 'stepwise' loss of ammonia (Biltz 1913, Wendlandt 1958). The compound readily aquates in hot water, forming aquopentamminecobalt (III) chloride (Schlessinger 1967). The aquation half-life is around 100 hours at temperatures of 25-35°C (Archer et al. 1965).

4.7-1 Separation procedures

Separation of the complex $[Co(NH_3)_5Cl]^{2+}$ from the anionic chlorine in the compound $[Co(NH_3)_5Cl]Cl_2$ was achieved by ion exchange. Samples of ca. 25 mg of $[Co(NH_3)Cl]Cl_2$ were each dissolved in 25 ml of water and aliquots of 10 ml taken to determine the total activity in the sample. The remaining 15 ml of each sample were transferred to a 100-ml separatory funnel containing 10 ml of cationic resin, Amberlite IR-120 (H). The mixture was shaken until the solution was colourless indicating removal of $[Co(NH_3)_5Cl]^{2+}$ from solution. The liquid phase was separated, the resin was carefully washed and all liquids were combined for counting as the anionic fraction. The activity of the cationic side was obtained from the difference between the total activity and that measured for the anionic fraction.

To determine whether this procedure led to a complete separation of the two species, the chloride content of the anionic fraction was determined by Volhard's method (Vogel 1961). The analysis showed that 99.8 ± 0.4% of the chloride present in the anionic side of the compound $[Co\ (NH_3)Cl]Cl_2$ was contained in the liquids separated from the resin.

4.7-2 Selection tests

(i) Zero-time exchange

The percentages of exchange were measured in samples A and B (see chapter 3, section 3.5-2) of the compound labelled in the anionic side and in a sample of the compound labelled in the cationic side (sample C). These measurements, made after the separation of the two species and before any further treatment was given to the samples, gave the following results:

$$E'_{oA} = 10.3 \pm 0.8\%$$

$$E'_{oB} = 2.0 \pm 0.9\%$$

$$E'_{oC} = 0.1 \pm 0.5\%$$

The different values for the zero-time exchange are probably due to the differences in the procedures used to obtain the labelled samples.

(ii) Sample treatments.

a) Thermal treatment. Samples of approximately 25 mg of the labelled compound were heated at constant temperatures in the range 90-180°C for 1 hour and 10 minutes. This treatment induced some exchange between the chlorines present in the cationic and anionic sides of $[Co(NH_3)Cl]Cl_2$ and a thermogravimetric analysis of the compound was done in order to determine the highest temperature which could be used before decomposition set in.

(iii) Decomposition analysis. A sample of 8.92 mg of $[Co(NH_3)_5Cl]Cl_2$ was analysed thermogravimetrically, being heated at 5°C/min in a flux of nitrogen and using an automatic thermobalance manufacturered by Stanton-Redcroft.

The thermal decomposition curve is shown in Figure 4.3. As can be seen, no loss of weight occurred until a temperature of 174°C was reached. Beyond this temperature the compound started to lose weight and to decompose.

This agrees with the result reported by Wendlandt (1958) who obtained a temperature of 170°C. Biltz (1913) found that chloropentamminecobalt (III) chloride decomposes at 180-220°C.

4.7-3 Conclusion

Since the thermogravimetric analysis showed that there is no decomposition before 170°C, the compound $[Co(NH_3)_5Cl]Cl_2$ was considered suitable for the study of the solid-state exchange

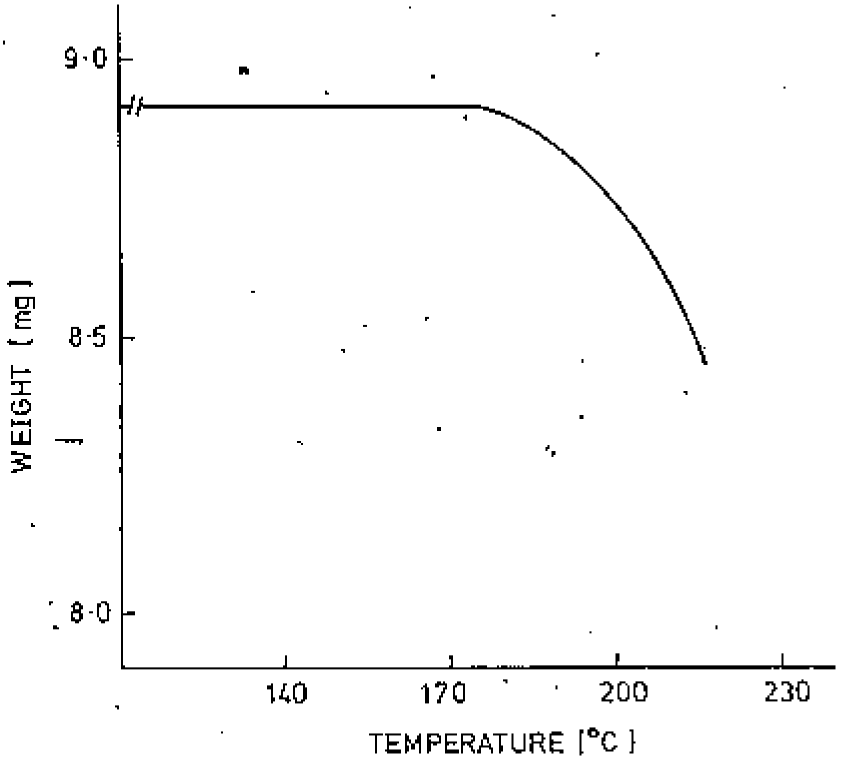

Fig. 4.3 The thermal decomposition curve for $[Co(NH_3)_5Cl]Cl_2$.

reaction between the chlorine atoms lying in the anionic and cationic sides of the compound. Other treatments, such as gamma irradiation and crushing, were also given to the labelled samples, results of which are presented in chapter 6.

4.8 $Cr_2(C_2O_4)_3.6H_2O$ - chromium (III) oxalate hexahydrated

A good choice for the study of the mechanisms by which exchange reactions take place in the solid state is the chromium (III) oxalates, both because of the many possible complexes like $[Cr(C_2O_4)(H_2O)_4]^+$, $[Cr(C_2O_4)_2(H_2O)_2]^-$ and $[Cr(C_2O_4)_3]^{3-}$, and because of the advantageous nuclear properties of ^{51}Cr (Lederer *et al*. 1967):

Radioactive isotope	Half-life	Major radiations* approximate energies (MeV) and intensities
^{51}Cr	27.8 d	γ vx-rays, 0.320 (9%) e^- 0.315

Kawamura and Wada (1957) studied the exchange in solution between the chromium atoms in the compound $[Cr(C_2O_4)(H_2O)_4]$ $[^{51}Cr(C_2O_4)_2(H_2O)_2]$. They observed how the distribution of radioactivity changed with time and pH, indicating a transition of oxalate from the anionic to the cationic part of the compound.

The formation of the dioxalatodiaquochromate (III) ion from hexaquochromium (III) and oxalate ions was studied by Hamm and Davis (1953) and the kinetics of aquation of the trisoxalatochromium (III) ion was studied by Khrishnamurty and Harris (1960).

Cis-trans isomerism is observed in the $[Cr(C_2O_4)_2(H_2O)_2]^-$

ion. The kinetics of isomerization of the trans isomer into the cis form, and of the racemization of the optically-active cis complex in aqueous solution, have both been investigated (Hamm 1953, Hamm & Perkins 1955, Hamm *et al*. 1961, Welch & Hamm 1963).

4.8-1 Separation procedures

The separation of the chromium (III) species in both the compounds $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ and $[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$ was achieved by ion-exchange using the resin Zerolit-225 (H) chromatographic grade; the ion-exchange tube was 30 cm long and of 12 mm internal diameter.

Samples of approximately 30 mg of $[Cr(H_2O)_6][Cr(C_2O_4)_3]$, and 150 mg of $[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$ were used in each separation. A larger quantity of the second compound was necessary due to its lower specific activity. The samples were dissolved in 50 ml of water and aliquots of 10 ml taken to determine the total activity of each. The other 40 ml were percolated through the column of resin. The eluate was collected and the resin carefully washed. The resulting solution was concentrated to a volume of 25 ml, 10 ml of which was counted as the anionic fraction.

The chromium content of the eluate was determined by titration with standard ferrous solution, after oxidation to dichromate by boiling with excess ammonium persulphate in the presence of silver nitrate as catalyst (Vogel 1961): this was to check that the separation of the two chromium species was complete.

The separation of $[Cr(C_2O_4)(H_2O)_4]^+$ from $[Cr(C_2O_4)_2(H_2O)_2]^-$

was found to be complete when a 0.1-0.2% solution of the compound was percolated at a rate no faster than 0.5 ml/minute through the column. The separation of $[Cr(H_2O)_6]^{3+}$ from $[Cr(C_2O_4)_3]^{3-}$ was favoured by the great affinity of the resin for $[Cr(H_2O)_6]^{3+}$.

4.8-2 Selection tests

(i) Zero-time exchange

The measurements of the exchange percentages in the two chromium (III) oxalates, both labelled in the cationic side, were made after separation and before thermal treatment, and they gave the following values:

$$E'_{o1} = 9.2 \pm 0.5\% \; ([^{51}Cr(H_2O)_6][Cr(C_2O_4)_3])$$

and $E'_{o2} = 14.5 \pm 0.8\%$ ($[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$).

These values were considered low enough to allow the exchange reaction in the solid state to be studied. The following test was therefore carried out:

(ii) Sample treatments

a) Thermal treatment. Samples of both compounds were sealed in glass ampoules and heated for 2 hours in an air oven at temperatures between 30 and 110°C. It was observed that thermal treatment induced exchange in both compounds and that the exchange process was related to the transformations occurring in the compounds due to thermal treatment.

(iii) Decomposition analysis

a) $[Cr(H_2O)_6][Cr(C_2O_4)_3]$. It was observed that heating induced the decomposition of $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ into

$[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$. The extent of decomposition was determined in samples of known weight, heated for 2 hours in sealed ampoules at 50°C and 100°C.

The cationic and anionic fractions of the compound were first separated according to the method described in section 4.8-1, using a cation-exchange column of resin. Then the species $[Cr(C_2O_4)(H_2O)_4]^+$ was eluted with 0.05 N $HClO_4$ and the content of chromium was determined in the eluate by titration with potassium dichromate (Vogel 1961). The results expressed as percentages of decomposition were:

50°C : 12.8 ± 0.8 %

100°C : 44.5 ± 0.9 %

The extent of decomposition was also determined by counting the activity present in the species $[^{51}Cr(C_2O_4)(H_2O)_4]^+$ and comparing it with the activity that should have been in the $[^{51}Cr(H_2O)_6]^{3+}$ form if there had been no decomposition. The results expressed as percentage of decomposition, D%, were:

T (°C)	20	32	50	64	74	90	100	110
D (%)	11.6	11.8	12.7	12.7	29.1	30.4	35.4	74.2

It was observed that the compound $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ was unstable when in contact with air. A sample that was left in an opened vessel for 10 days showed 51.3% of decomposition.

b) $[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$. This compound is also not very stable, decomposing at temperatures around 80°C with the formation of $[Cr(C_2O_4)_3]^{3-}$.

4.8-3 Conclusion

Considering that it was possible to follow the exchange reaction in the chromium oxalates in spite of the processes of decomposition induced by thermal treatment, further investigations were carried out on these compounds. These experiments are described in chapter 7.

CHAPTER 5 - EXCHANGE STUDIES ON $[Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3 \cdot H_2O$

CHAPTER 5 - EXCHANGE STUDIES ON $[Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3 \cdot H_2O$

In this chapter the experimental data resulting from the study of the exchange reaction between the iron atoms lying in the cationic and anionic sites of the solid compound $[^{59}Fe(H_2O)_6]$ $[Fe\ EDTA\ (H_2O)]_3 \cdot H_2O$ is discussed. The data are treated mathematically in order to define the most probable number of reactions, the energies of activation and the proportions of every reaction occurring with different energies (see chapter 2, section 2.3).

The transfer of radioactivity induced by thermal treatment was followed by measuring the fraction of exchange, either as a function of temperature (isochronal) for a constant period of time (2.25 hrs), or as a function of time (up to 30 hrs at 100°C; 20 hrs at 110, 120°C) at a constant temperature (isothermal). All the samples were heated in sealed glass ampoules, with exception of one experiment as discussed in the text.

The experimental results are expressed in terms of the percentage of exchange, corrected for the apparent zero-time exchange (see section 4.2, chapter 4). The error stated is the standard deviation from the mean value when more than one determination was carried out on a given sample.

5.1 Experimental results

5.1-1 The effects of different methods of preparation on the exchange reaction

The results obtained from an isochronal heating of samples A and B are shown in Tables 5.1 and 5.2, respectively, and

Table 5.1 Isochronal heating of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3 .H_2O$. Sample A. Time: 2 h 15 min

Temperature T (^oC)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
100	0.1	99.9
110	0.7 ± 0.2	99.3 ± 0.2
120	4.3 ± 0.7	95.7 ± 0.7
127	15.6 ± 1.7	84.4 ± 1.7
130	28.9 ± 1.1	71.1 ± 1.1
135	32.5 ± 0.5	67.5 ± 0.5
140	35.1 ± 2.5	64.9 ± 2.5
150	49.9 ± 0.2	50.1 ± 0.2

Table 5.2 Isochronal heating of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3 \cdot H_2O$

Sample B. Time: 2 h 15 min

Temperature T (°C)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
100	0.1	99.9
112	3.2 ± 1.4	96.8 ± 1.4
120	4.9	95.1
125	9.3 ± 1.2	90.7 ± 1.2
130	9.4 ± 0.9	90.6 ± 0.9
135	20.7 ± 1.2	79.3 ± 1.2
140	25.6 ± 2.1	74.4 ± 2.1
150	39.6	60.4

presented graphically in Figure 5.1 where the values resulting from the analysis of the decomposition of the compound (see chapter 4, section 4.6-2) are also plotted. It can be seen that the different methods of preparation led to different exchange isochronal curves. Therefore all other experiments were made using only one of the preparations: sample B.

The results of the isothermal measurements on sample B are shown in Table 5.3 and Figure 5.2.

5.1-2 The effect of gamma-irradiation

A bulk sample of the labelled compound was irradiated with γ rays up to a total dose of 5 Mrad. Since it was observed that the irradiation by itself failed to induce exchange, portions of the irradiated sample were submitted to an isochronal treatment. The results are shown in Table 5.4 which also contains a column showing the results for the untreated sample. In Figure 5.3 the isochronal curves for both the irradiated and the untreated samples are presented. It can be seen that the irradiation also failed to promote a subsequent thermal exchange.

A spectrophotometric analysis of the irradiated sample showed that no decomposition due to the irradiation had occurred.

5.1-3 The effect of crushing

A sample of the compound was crushed to a very fine powder and the exchange followed by isochronal and isothermal heatings. The results for the isochronal exchange experiments are presented in Table 5.5 which also includes the results for the untreated sample, and the isochronal curves are plotted in Figure 5.4.

Table 5.6 shows the results for the isothermal-exchange

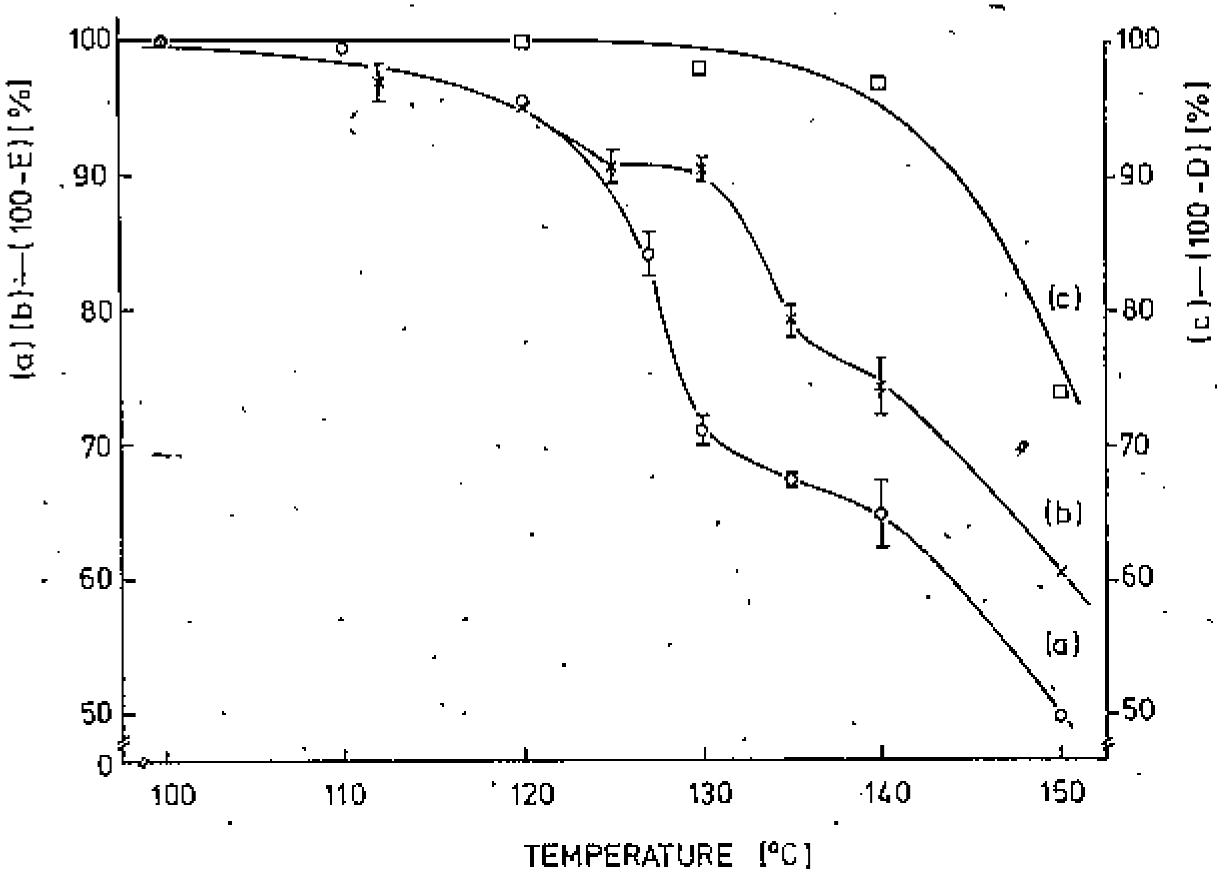

Fig. 5.1 The exchange isochronals of $[^{59}Fe(H_2O)_6]$ $[Fe\ EDTA\ (H_2O)]_3 \cdot H_2O$. Time: 2 h 15 min.
O : sample A (curve a); X : sample B (curve b).
The thermal decomposition curve (ordinate on the right side). ☐ : undecomposed fraction (curve c).

Table 5.3 Isothermal heating of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3 \cdot H_2O$

Sample B.

Temperature T (°C)	Period of heating t (hours)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
100	2	0.3	99.7
	5	5.6 ± 2.4	94.4 ± 2.4
	10	12.0 ± 0.5	88.0 ± 0.5
	15	14.5 ± 1.5	85.5 ± 1.5
	20	16.2	83.8
	30	22.7 ± 2.8	77.3 ± 2.8
110	2	3.2	96.8
	5	12.9 ± 1.1	87.1 ± 1.1
	10	27.6 ± 1.4	72.4 ± 1.4
	15	33.7 ± 2.3	66.3 ± 2.3
	20	43.4	56.6
120	2	4.9	95.1
	5	16.7 ± 1.0	83.3 ± 1.0
	10	31.8 ± 1.2	68.2 ± 1.2
	15	44.9 ± 2.1	55.1 ± 2.1
	20	51.2 ± 3.7	48.8 ± 3.7

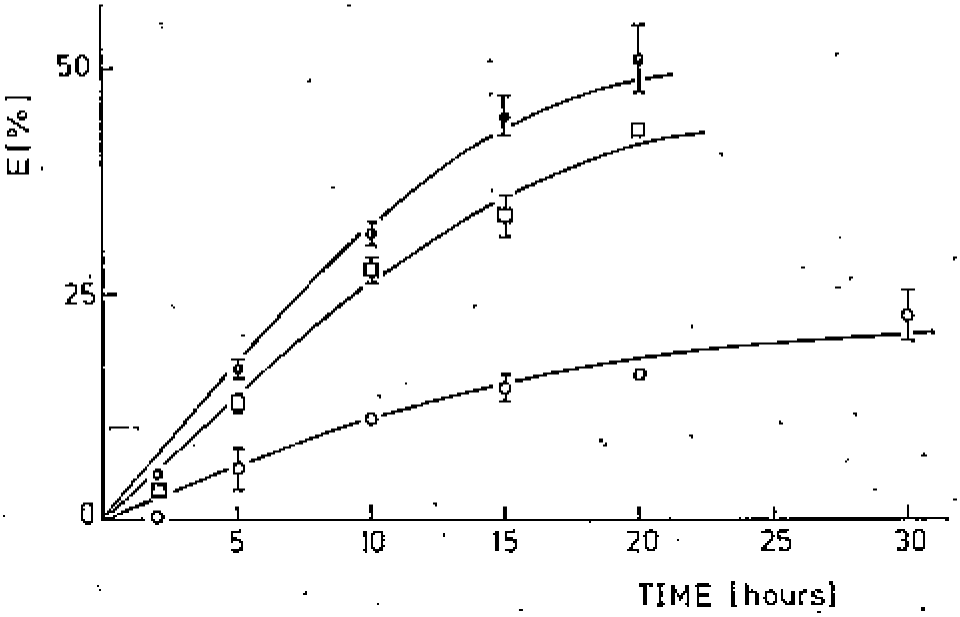

Fig. 5.2 The exchange isothermals of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3$ $.H_2O$. Sample B.

O : 100°C ; □ : 110°C ; ⊙ : 120°C.

Table 5.4 Isochronal heating of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3\cdot H_2O$

Gamma-irradiated sample (5 Mrad). Sample B. Time: 2 h 15 min

The last column contains the unexchanged fraction in the untreated sample for comparison.

	γ-irradiated sample		Untreated sample
Temperature T (°C)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)	Unexchanged fraction (100-E) (%)
100	1.0	99.0	99.9
112	1.8	98.2	96.8 ± 1.4
120	6.6 ± 1.1	93.4 ± 1.1	95.1
125	-	-	90.7 ± 1.2
130	9.6 ± 2.7	90.4 ± 2.7	90.6 ± 0.9
135	-	-	79.3 ± 1.2
140	24.8	75.2	74.4 ± 2.1
150	41.4	58.6	60.4

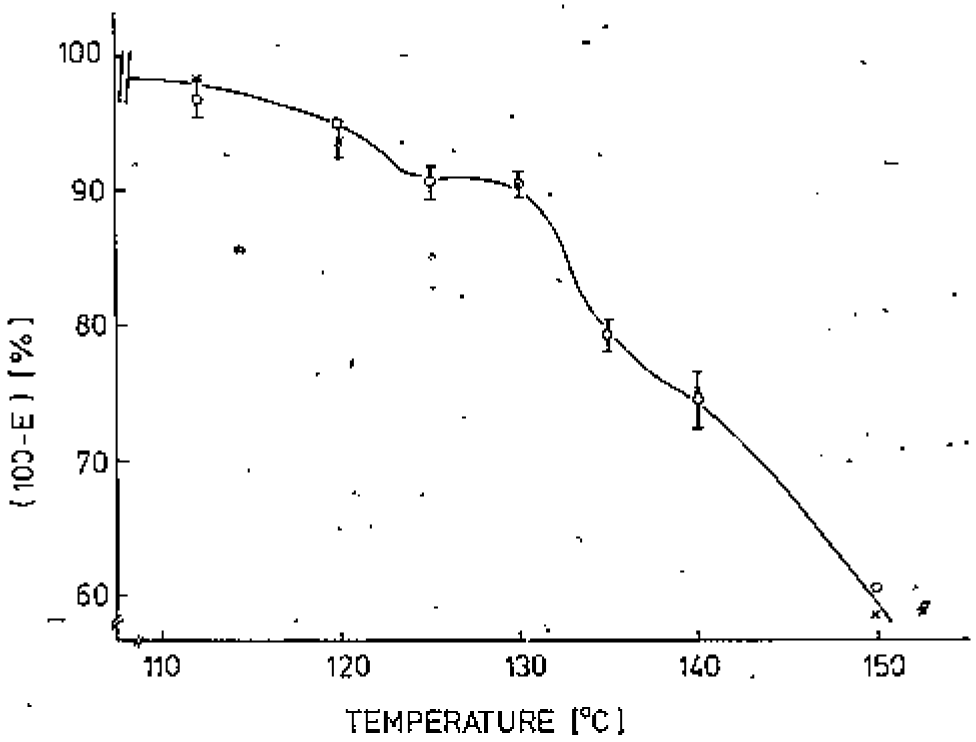

Fig. 5.3 The exchange isochronals of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3$ $.H_2O$. Sample B. Time: 2 h 15 min.

X : γ-irradiated sample (5 Mrad)

O : untreated sample

Table 5.5 Isochronal heating of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3 \cdot H_2O$ Sample B. Crushed sample. Time: 2 h 15 min. The last column contains the unexchanged fraction in the untreated sample for comparison.

	Crushed sample		Untreated sample
Temperature T (°C)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)	Unexchanged fraction (100-E) (%)
80	4.0	96.0	–
90	6.8	93.2	–
100	11.0 ± 1.2	89.0 ± 1.2	99.9
110	12.0 ± 0.7	88.0 ± 0.7	–
112	–	–	96.8 ± 1.4
115	19.4 ± 1.0	80.6 ± 1.0	–
120	30.3 ± 1.7	69.7 ± 1.7	95.1
125	–	–	90.7 ± 1.2
130	35.4	64.6	90.6 ± 0.9
135	–	–	79.3 ± 1.2
140	37.5 ± 4.4	62.5 ± 4.4	74.4 ± 2.1
150	41.8	58.2	60.4

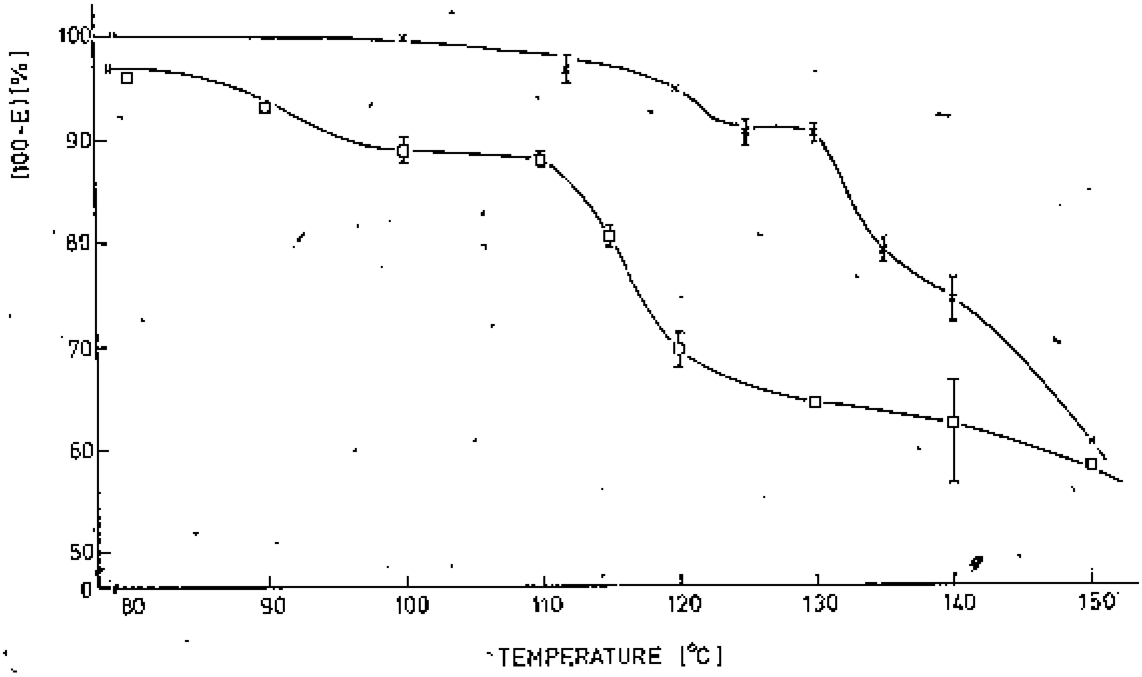

Fig. 5.4 The exchange isochronals of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3$ $.H_2O$. Sample B. Time: 2 h 15 min.

☐ : crushed sample

X : untreated sample

Table 5.6 Isothermal heating of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3.H_2O$ Crushed sample. Sample B. The last column contains the unexchanged fraction in the untreated sample for comparison.

		Crushed sample		Untreated sample
Temperature T (°C)	Period of heating t (hours)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)	Unexchanged fraction (100-E) (%)
100	2	11.0	89.0	99.7
	5	36.5 ± 1.5	63.5 ± 1.5	94.4 ± 2.4
	10	47.2 ± 0.5	52.8 ± 0.5	88.0 ± 0.5
	15	47.3	52.7	85.5 ± 1.5
	20	46.0 ± 1.7	54.0 ± 1.7	83.8
	30	47.7	52.3	77.3 ± 2.8
120	2	30.3 ± 1.8	69.7 ± 1.8	95.1
	5	48.4 ± 2.4	51.6 ± 2.4	83.3 ± 1.0
	10	48.2	51.8	68.2 ± 1.2
	15	48.8	51.2	55.1 ± 2.1
	20	49.7 ± 2.7	50.3 ± 2.7	48.8 ± 3.7

experiments which are presented graphically in Figure 5.5. In both the table and the figure, the results for the crushed sample can be compared with those for the untreated sample.

It can be seen from these experiments that crushing the crystals before heating enhanced the subsequent thermal exchange.

5.1-4 The effect of dehydration

Exchange had been observed in a range of temperature where dehydration also occurs; the following experiments were therefore carried out to observe the influence of dehydration on the exchange behaviour.

A sample of the untreated compound was dehydrated by heating at 95°C under vacuum. The fraction of exchange measured afterwards indicated that the dehydration by itself had no influence on exchange. The dehydrated sample was then submitted to an isochronal heating. The results obtained are shown in Table 5.7 where they can be compared with those for the untreated sample.

Another isochronal experiment was performed in which hydrated samples were heated in opened ampoules to observe the effect of dehydration during the isochronal heating; in this case the water liberated during dehydration could escape from the ampoule. The results from this experiment are shown in Table 5.8 where they can be compared with those for the hydrated samples heated in sealed ampoules and with those for the previously-dehydrated sample. The curves are plotted in Figure 5.6.

It can be seen that the results for the dehydrated sample and for the hydrated samples heated in opened ampoules are the

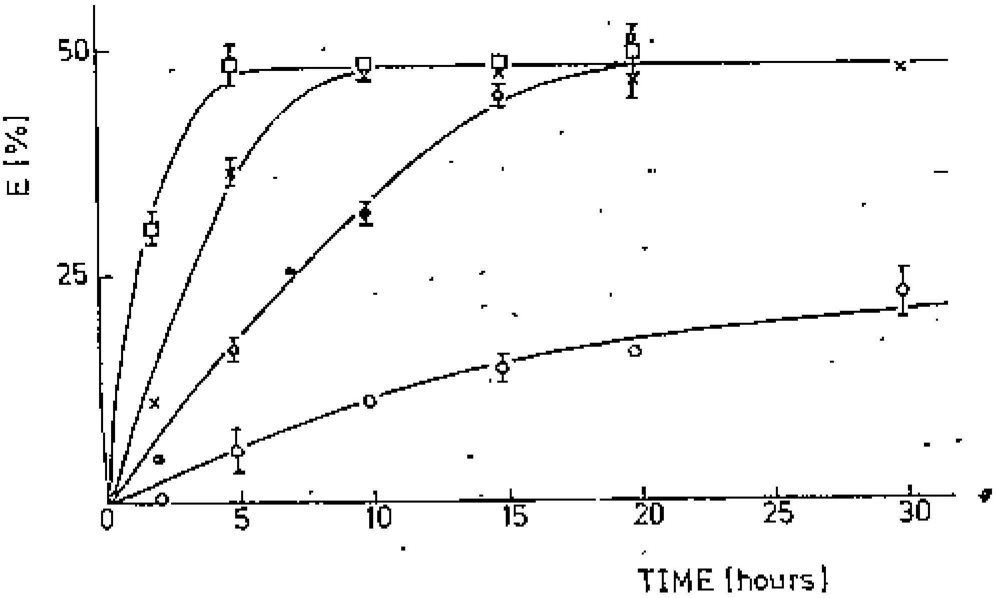

Fig. 5.5 The exchange isothermals of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3$ $.H_2O$. Sample B.

□ : 120°C, crushed sample

⊖ : 120°C, untreated sample

X : 100°C, crushed sample

O : 100°C, untreated sample

Table 5.7 Isochronal heating of $[^{59}Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3 \cdot H_2O$. Sample B. Dehydrated sample. Time:2 h 15 min. The last column contains the unexchanged fraction in the untreated sample for comparison.

	Dehydrated sample		Untreated sample (hydrated)
Temperature T (°C)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)	Unexchanged fraction (100-E) (%)
100	-	-	99.9
110	0.1	99.9	-
112	-	-	96.8 ± 1.4
120	0.5	99.5	95.1
125	3.3 ± 0.5	96.7 ± 0.5	90.7 ± 1.2
130	4.1	95.9	90.6 ± 0.9
135	4.3 ± 0.6	95.7 ± 0.6	79.3 ± 1.2
140	8.1 ± 1.8	91.9 ± 1.8	74.4 ± 2.1
150	24.7 ± 2.8	75.3 ± 2.8	60.4

Table 5.8 Isochronal heating of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3.H_2O$. Untreated sample heated in opened ampoule. Sample B. Time: 2 h 15 min. The unexchanged fraction for the untreated sample heated in sealed ampoules and for the previously dehydrated sample are also given for comparison.

	Untreated sample (hydrated)			Dehydrated sample
	Opened ampoule		Sealed ampoule	
Temperature T (°C)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)	Unexchanged fraction (100-E) (%)	Unexchanged fraction (100-E) (%)
100	-	-	99.9	-
110	0.2	99.8	-	99.9
112	-	-	96.8 ± 1.4	-
120	0.5	99.5	95.1	99.5
125	3.4 ± 1.1	96.6 ± 1.1	90.7 ± 1.2	96.7 ± 0.5
130	4.7 ± 1.0	95.3 ± 1.0	90.6 ± 0.9	95.9
135	5.4 ± 0.8	94.6 ± 0.8	79.3 ± 1.2	95.7 ± 0.6
140	8.4	91.6	74.4 ± 2.1	91.9 ± 1.8
150	24.2	75.8	60.4	75.3 ± 2.8

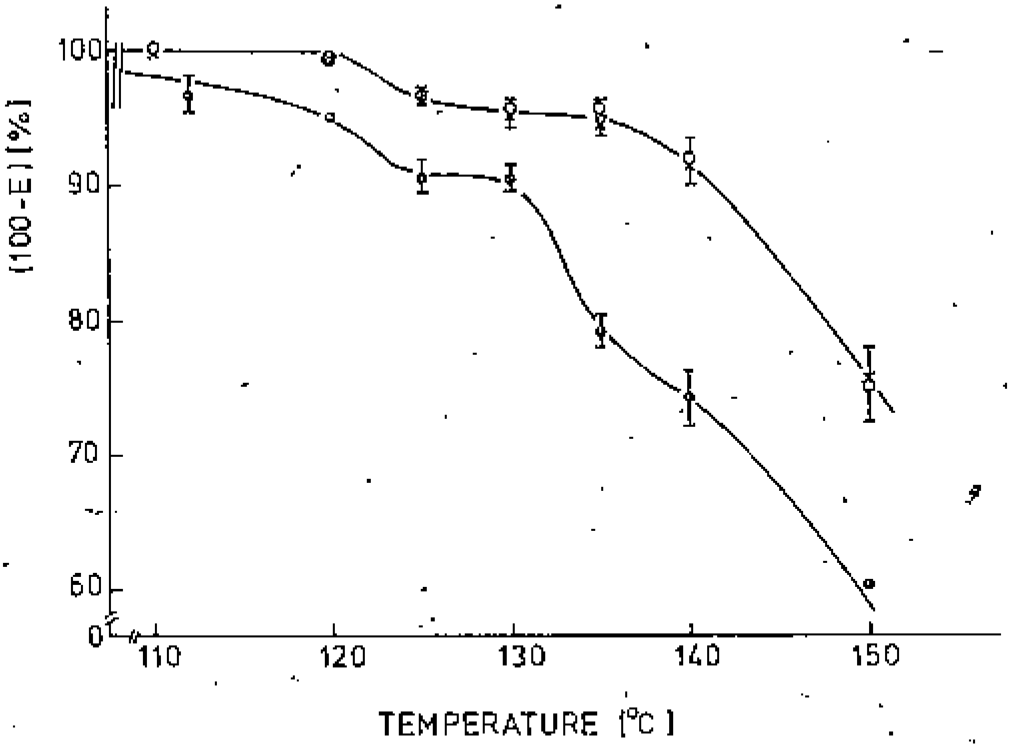

Fig. 5.6 The exchange isochronals of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3 \cdot H_2O$. Sample B. Time: 2 h 15 min.

O : dehydrated sample

X : untreated sample (hydrated) heated in opened ampoules

⊙ : untreated sample (hydrated) heated in sealed ampoules same. These results are however lower than the ones for the hydrated samples heated in sealed ampoules.

5.2 Mathematical treatment of the experimental data

The experimental data were analysed using a computer. The data describing the progress of the reaction obtained at several times and temperatures were fitted by a model in which one or more reaction paths were available with different activation energies and probabilities (see chapter 2, section 2.3).

Equation (2.6) was solved supposing one, two and three reaction paths were available:

$$1 - F = \sum_i P_i e^{-\lambda_i t} \qquad (2.6)$$

The smallest number of reaction paths consistent with a good fit to the experimental data was used.

Figure 5.7 shows a semi-logarithmic plot of the unexchanged fraction against time for the exchange isothermals, from which it can be seen that the transfer of radioactivity involves more than one reaction path, a conclusion already suggested by the structured shape of the isochronal curve presented in Figure 5.1. The total unexchanged fraction was taken either from the isochronal measurements or the isothermal measurements or both.

The value of υ for solid compounds is known to be $\approx 10^{13}\,s^{-1}$ (Brown et al. 1953). Different values of υ varying between 10^9 and 10^{16} were tried, the value giving the best fit to each set of data being chosen.

The results of this mathematical treatment applied to untreated samples of A and B are shown in Table 5.9. The

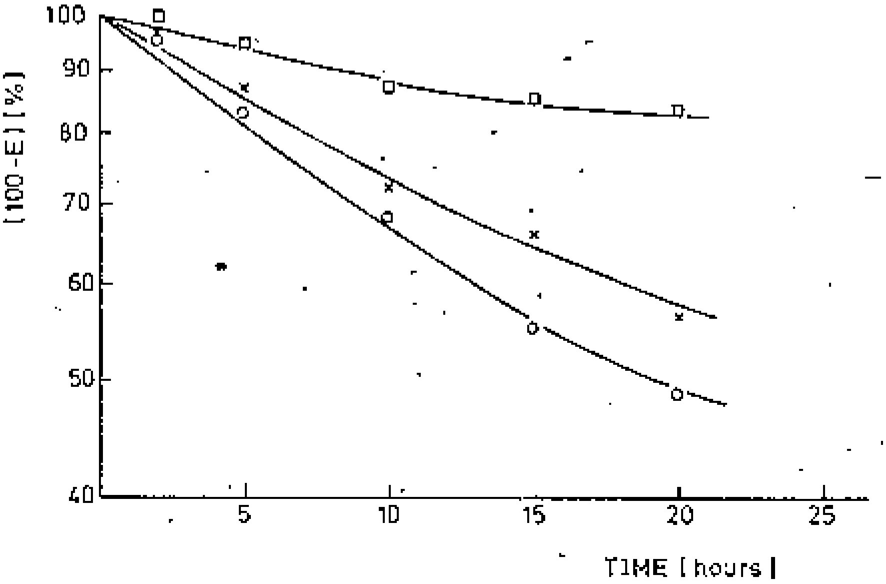

Fig. 5.7 The exchange isothermals of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)_3]_3$ $.H_2O$. Sample B.

□ : 100°C ; X : 110°C ; O : 120°C

Table 5.9 The results of the mathematical analysis. Samples A and B of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3.H_2O$. Untreated samples

	Sample A (untreated)		Sample B (untreated)					
	Isochronal data		Isochronal data		Isothermal data		Isochronal + Isothermal data	
	Energy of activation E_a(eV)	Proportion P (%)	Energy of activation E_a(eV)	Proportion P (%)	Energy of activation E_a(eV)	Proportion P (%)	Energy of activation E_a(eV)	Proportion P (%)
One reaction path	1.728	100.00	1.725	100.00	1.667	100.00	1.696	100.00
Two reaction paths	1.655	50.22	1.670	38.14	1.557	14.15	1.567	17.56
	2.941	49.78	1.830	61.86	1.691	85.85	1.751	82.44
Three reaction paths			1.532	1.47			1.548	12.16
	-	-	1.678	40.77	-	-	1.669	27.44
			2.850	57.76			2.928	60.40
Frequency factor ν (s^{-1})	2.5×10^{16}		2.5×10^{16}		2.5×10^{16}		2.5×10^{16}	

calculated and measured curves may be compared in Figures 5.8 (isochronal) and 5.9 (isothermal).

Table 5.10 presents the results of the mathematical treatment applied to the isochronal data of the dehydrated and untreated samples. It can be seen that dehydration changed not only the energies of activation and the proportions exchanging by the different reaction paths, but also the number of paths available for exchange. These results are also plotted in Figure 5.10.

Table 5.11 shows the results of the mathematical treatment applied to the isochronal data for the crushed and untreated samples. It can be seen that crushing the crystals before heating affected the values of the energies of activation and the proportions of the various reactions. These results are plotted in Figure 5.11.

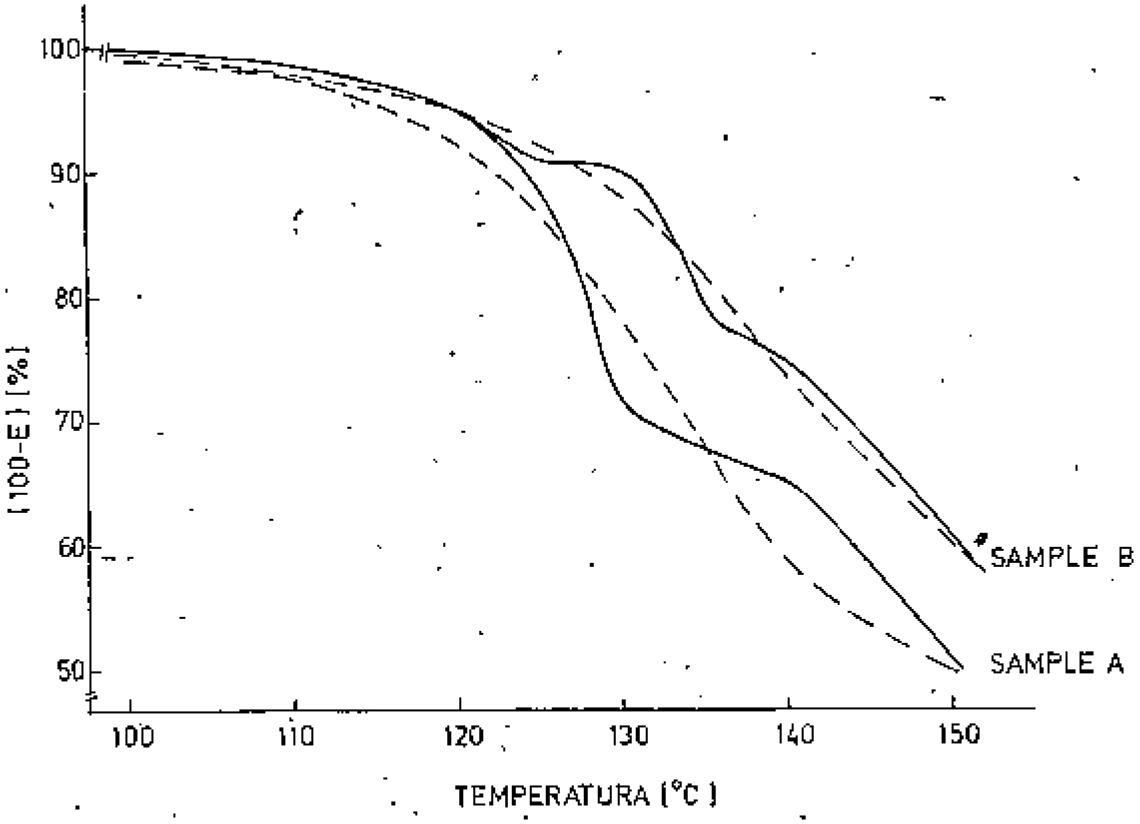

Fig. 5.8 The exchange isochronals of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3 \cdot H_2O$. Samples A and B. Time: 2 h 15 min.

Experimental curves ; ———

Calculated curves: ------

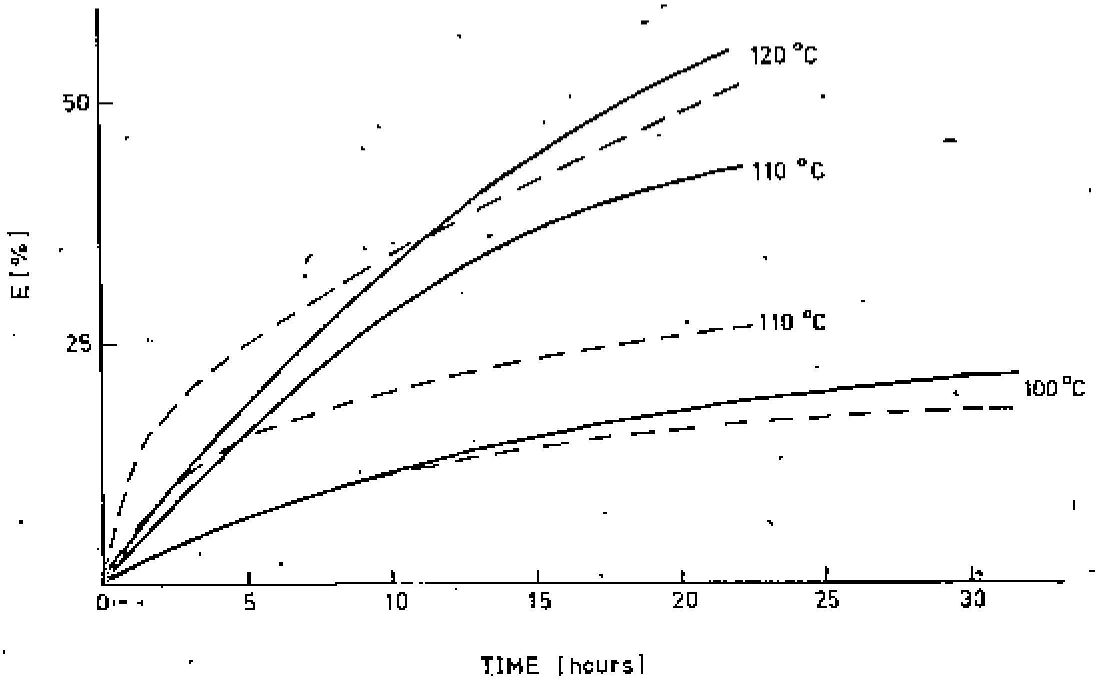

Fig. 5.9 The exchange isothermals of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3$ $.H_2O$. - Sample B.

Experimental curves : ———

Calculated curves: ------

Table 5.10 The results of the mathematical analysis for Sample B of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3.H_2O$ Dehydrated sample. The last column contains the results for the untreated sample for comparison.

	Dehydrated sample		Untreated sample	
	Isochronal data		Isochronal data	
	Energy of activation E_a (%)	Proportion P (%)	Energy of activation E_a (%)	Proportion P (%)
One reaction path	1.759	100.00	1.725	100.00
Two reaction paths	1.569	1.73	1.670	38.14
	1.771	98.27	1.830	61.86
Three reaction paths	-	-	1.532	1.47
			1.678	40.77
			2.850	57.76
Frequency factor V (s^{-1})	2.5×10^{16}		2.5×10^{16}	

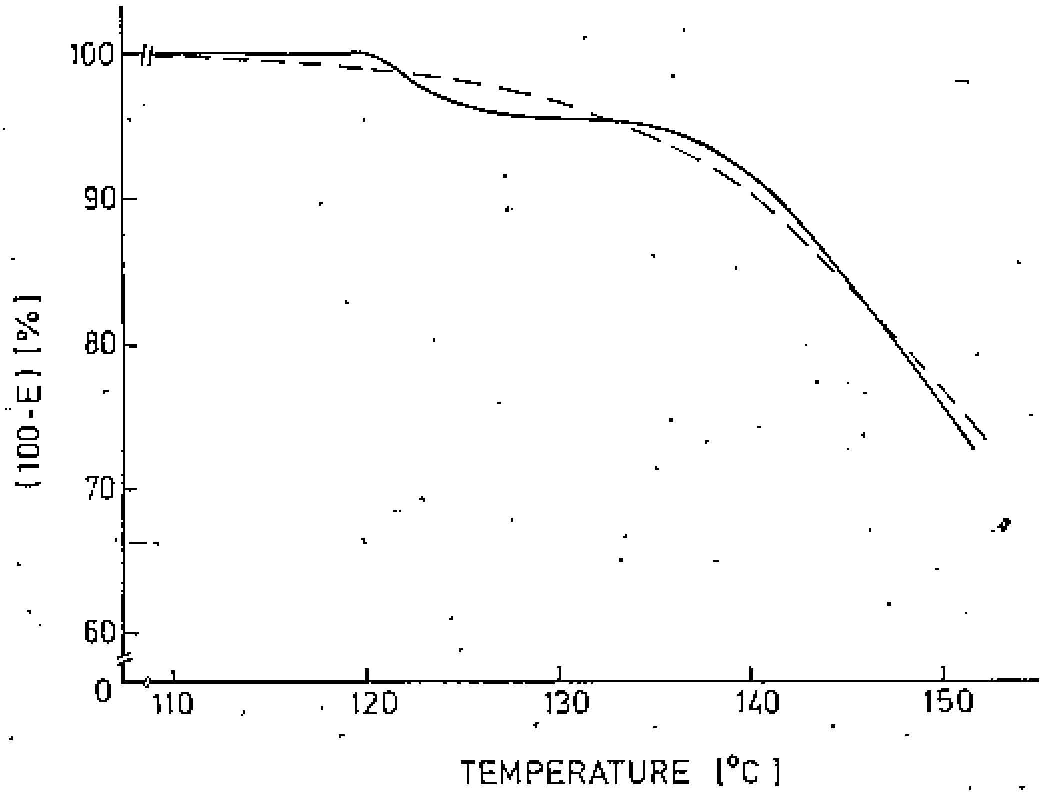

Fig. 5.10. The exchange isochronal of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3$ $.H_2O$. Sample B. Dehydrated sample. Time: 2 h 15 min

Experimental curve : ———

Calculated curve : ------

Table 5.11 The results of the mathematical analysis for Sample B of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3 \cdot H_2O$ Crushed sample. The last column contains the results for the untreated sample for comparison.

	Crushed sample		Untreated sample	
	Isochronal data		Isochronal data	
	Energy of activation E_a(eV)	Proportion P (%)	Energy of activation E_a(eV)	Proportion P (%)
One reaction path	1.720	100.00	1.725	100.00
Two reaction paths	1.576	35.09	1.670	38.14
	1.797	64.91	1.830	61.86
Three reaction paths	1.432	6.08	1.532	1.47
	1.588	30.01	1.678	40.77
	1.804	63.91	2.850	57.76
Frequency factor ν (s^{-1})	2.5×10^{16}		2.5×10^{16}	

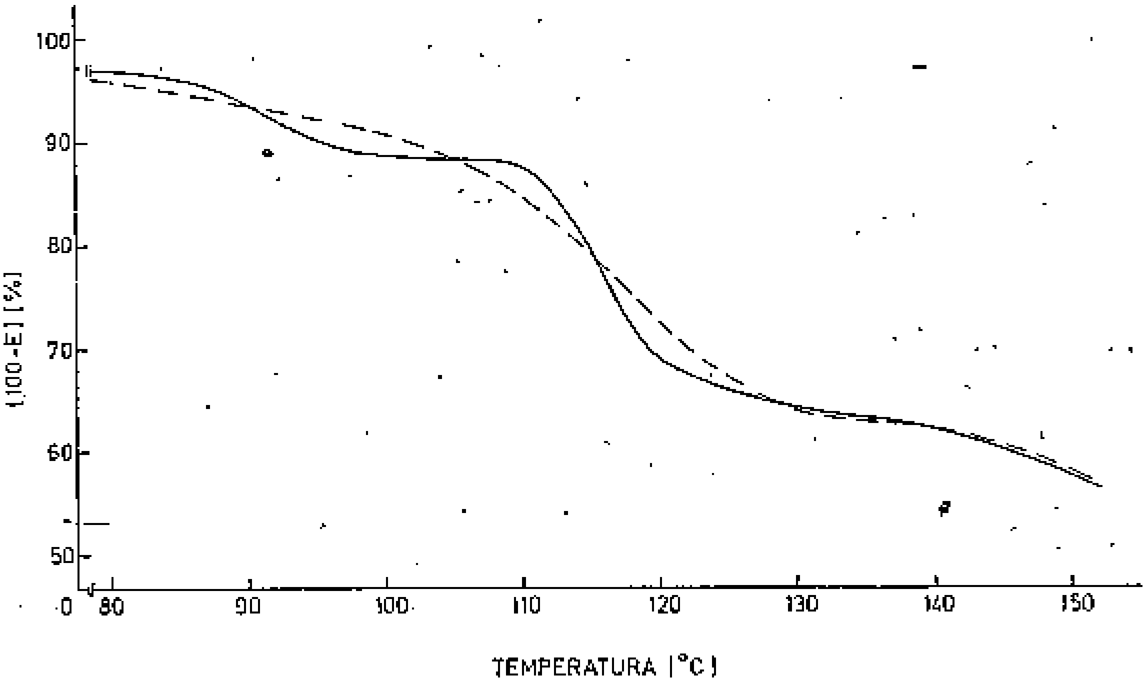

Fig. 5.11 The exchange isochronal of $[^{59}Fe(H_2O)_6][Fe\,EDTA\,(H_2O)]_3 \cdot H_2O$. Sample B. Crushed sample. Time: 2 h 15 min

Experimental curve : ———

Calculated curve : ------

CHAPTER 6 - EXCHANGE STUDIES ON $[Co(NH_3)_5Cl]Cl_2$

In this chapter, we present the results and an analysis of the experiments performed on the compound $[Co(NH_3)_5Cl]Cl_2$ to investigate the solid-state exchange reaction between the chlorine atoms lying inside and outside the coordination sphere.

Both isochronal and isothermal exchange measurements were made with samples of the compound prepared in different ways, labelled either in the cationic or the anionic sites. The period of heating in the isochronal measurements was 1 hour and 10 minutes. The experimental results are expressed as percentages of exchange, corrected for apparent zero-time exchanges as discussed in chapter 4, section 4.2. The errors given in the tables represent the standard deviations from the mean values when more than one determination was carried out on a given sample.

6.1 Experimental results

6.1-1 Exchange in $[Co(NH_3)_5Cl]^{36}Cl_2$

6.1-1.1 Isochronal treatment

Isochronal exchange measurements were performed on sample A of $[Co(NH_3)_5Cl]^{36}Cl$. The results obtained are shown in Table 6.1 and presented graphically in Figure 6.1.

6.1-1.2 The effect of gamma-irradiation on the exchange reaction

A portion of sample A was irradiated by γ-rays up to a total dose of 10 Mrad. The percentage of exchange just after the irradiation was measured, and it showed a value no bigger than

Table 6.1 Isochronal heating of $[Co(NH_3)_5Cl]^{36}Cl_2$. Time: 1 h 10 min. Sample A.

Temperature T (°C)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
90	1.7	98.3
100	1.5	98.5
110	2.3 ± 0.9	97.7 ± 0.9
120	5.7 ± 2.0	94.3 ± 2.0
130	5.6 ± 1.0	94.4 ± 1.0
140	9.9 ± 0.9	90.1 ± 0.9
150	10.5 ± 1.4	89.5 ± 1.4
160	17.8 ± 1.6	82.2 ± 1.6
170	26.2	73.8

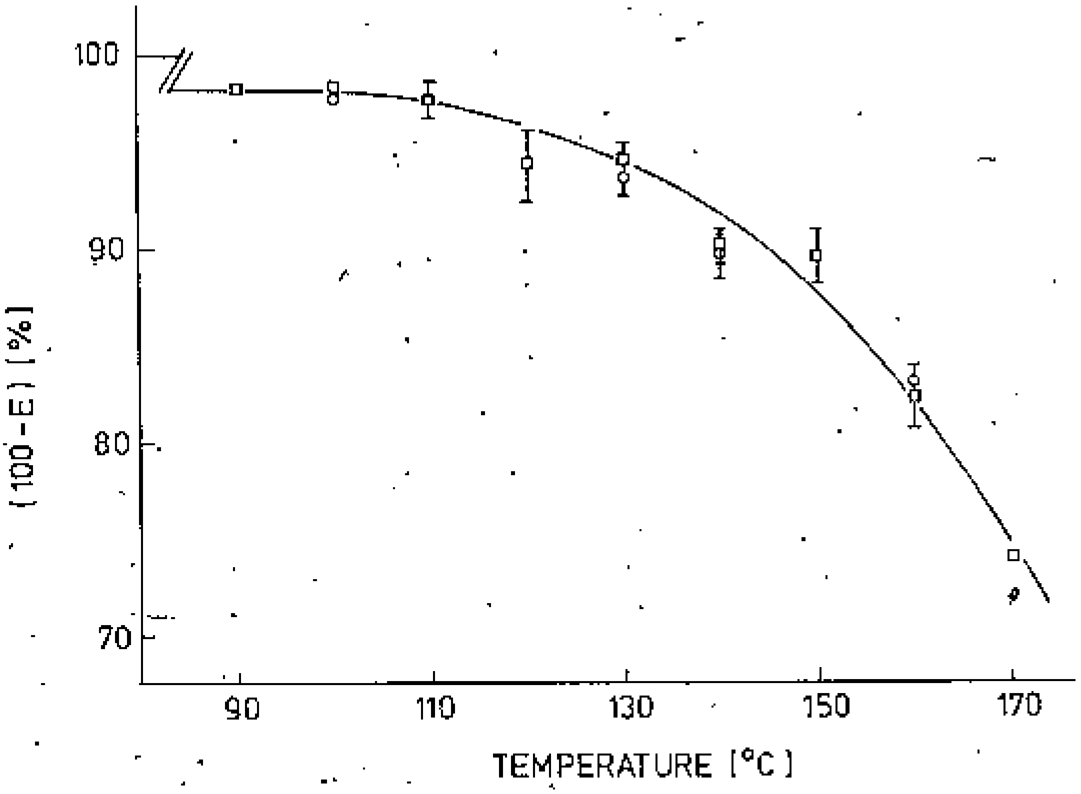

Fig. 6.1 The exchange isochronals of $[Co(NH_3)_5Cl]^{36}Cl_2$.

Sample A. Time: 1 h 10 min.

□ : untreated sample

O : γ-irradiated sample (10 Mrad).

the apparent zero-time exchange, indicating that the irradiation failed to induce exchange by itself.

Isochronal measurements were also made on the irradiated sample and the results are presented in Table 6.2 and in Figure 6.1 where they can be compared with those for the untreated sample. As can be seen, the irradiation failed also to stimulate subsequent thermal exchange.

In order to determine whether γ-irradiation induced decomposition, the concentration of solutions of irradiated and untreated samples was compared by spectrophotometry. The optical absorption of the solutions was measured in the 550-mμ waveband where $[Co(NH_3)_5Cl]^{2+}$ has an absorption peak. The analysis showed that no decomposition had been induced by a 10-Mrad γ-dose.

6.1-1.3 The effect of different methods of preparation

Sample A was prepared by a method which resulted in the compound being in fine powder form. Sample B was prepared using a slightly different method (see chapter 3, section 3.5-2) in order to obtain a crystalline form with larger crystals.

Isochronal exchange measurements were made on an untreated portion of sample B, and the experimental results are presented in Table 6.3 and in Figure 6.2, where they can be compared with the results for sample A. It can be seen that different preparations led to different results.

6.1-1.4 The effect of crushing

Crystals of sample B were crushed and submitted to isochronal heating. The results of the measurements are shown in Table 6.4 and in Figure 6.3. As can be seen, crushing the crystals

Table 6.2 Isochronal heating of $[Co(NH_3)_5Cl]^{36}Cl_2$. Sample A. Time: 1 h 10 min. γ-irradiated sample (10 Mrad). The last column contains the unexchanged fraction in the untreated sample for comparison.

	γ-irradiated sample		Untreated sample
Temperature T (°C)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)	Unexchanged fraction (100-E) (%)
90	-	-	98.3
100	2.4	97.6	98.5
110	2.4 ± 0.5	97.6 ± 0.5	97.7 ± 0.9
120	-	-	94.3 ± 2.0
130	6.5 ± 0.8	93.5 ± 0.8	94.4 ± 1.0
140	10.4 ± 1.2	89.6 ± 1.2	90.1 ± 0.9
150	10.6	89.4	89.5 ± 1.4
160	17.2	82.8	82.2 ± 1.6
170	-	-	73.8

Table 6.3 Isochronal heating of $[Co(NH_3)_5Cl]^{36}Cl_2$. Sample B. Time: 1 h 10 min. The unexchanged fractions for sample A are also given for comparison.

	Sample B		Sample A
Temperature T (°C)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)	Unexchanged fraction (100-E) (%)
90	-	-	98.3
100	0.3 ± 0.1	99.7 ± 0.1	98.5
110	-	-	97.7 ± 0.9
120	0.3	99.7	94.3 ± 2.0
130	1.3	98.7	94.4 ± 1.0
140	2.5 ± 0.5	97.5 ± 0.5	90.1 ± 0.9
150	3.6 ± 0.6	96.4 ± 0.6	89.5 ± 1.4
160	5.6 ± 1.2	94.4 ± 1.2	82.2 ± 1.6
170	5.9 ± 1.2	94.1 ± 1.2	73.8
180	10.3 ± 1.7	89.7 ± 1.7	-

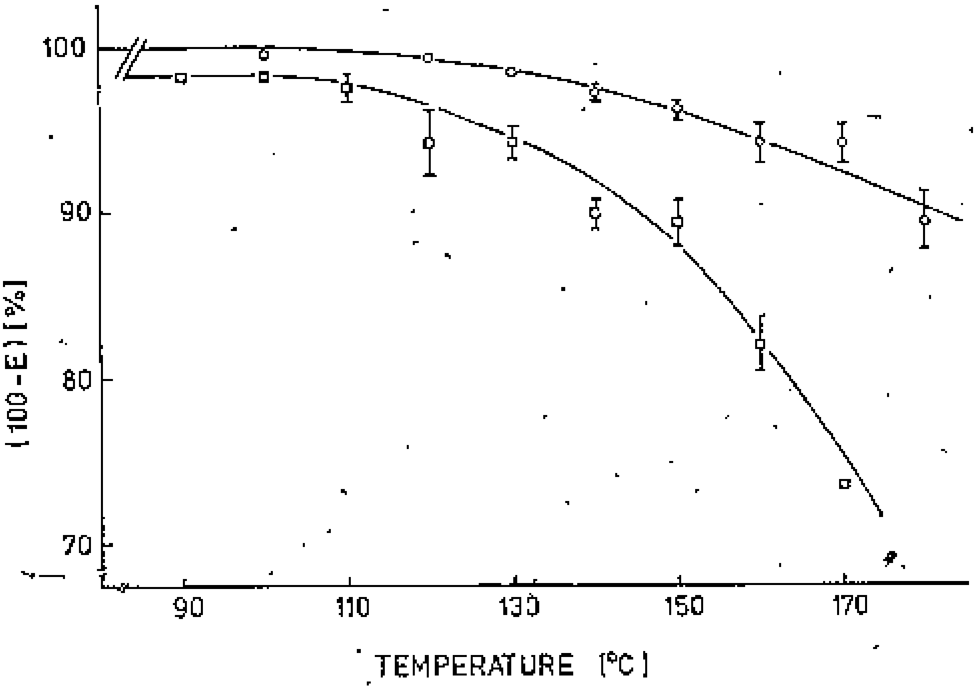

Fig. 6.2 The exchange isochronals of $[Co(NH_3)_5Cl]^{36}Cl_2$.

○ : sample B; □ : sample A

Untreated samples. Time: 1 h 10 min

Table 6.4 Isochronal heating of $[Co(NH_3)_5Cl]^{36}Cl_2$. Crushed sample. Sample B. Time: 1 h 10 min. The last column contains the unexchanged fraction in the untreated sample for comparison.

	Crushed sample		Untreated sample
Temperature T (°C)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)	Unexchanged fraction (100-E) (%)
100	0.2	99.8	99.7 ± 0.1
120	-	-	99.7
130	1.2	98.8	98.7
140	-	-	97.5 ± 0.5
150	3.9 ± 0.8	96.1 ± 0.8	96.4 ± 0.6
160	5.6	94.4	94.4 ± 1.2
170	6.7 ± 1.3	93.3 ± 1.3	94.1 ± 1.2
180	8.6	91.4	89.7 ± 1.7

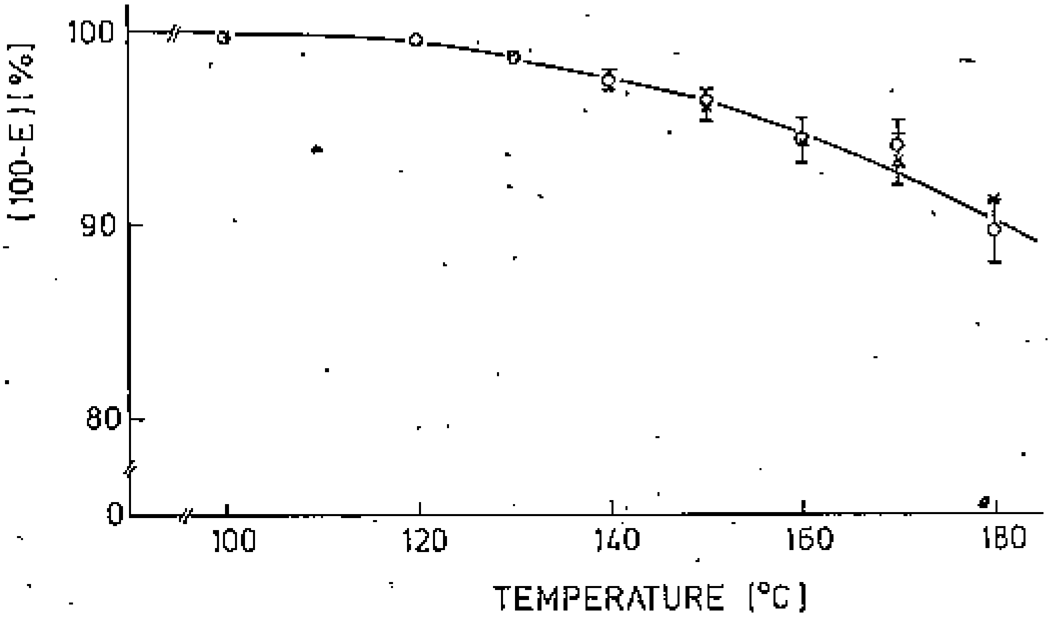

Fig. 6.3 The exchange isochronals of $[Co(NH_3)_5Cl]^{36}Cl_2$.

X : crushed sample

O : untreated sample

Sample B. Time: 1 h 10 min

before heating did not enhance the thermal exchange.

6.1-2 Exchange in $[Co(NH_3)_5{}^{36}Cl]Cl_2$

6.1-2.1 Isothermal treatment

The transfer of radioactivity was followed in a sample of the compound labelled in the cationic site, in order to check that exchange reactions were taking place. The results from isothermal measurements made at 160°C with samples of the compound labelled in the cationic side are presented in Table 6.5, and in the anionic side in Table 6.6. The isothermal curves are shown in Figure 6.4. These results confirm that the reaction observed was indeed an exchange reaction.

6.1-2.2 The effect of crushing

The effect of crushing on the exchange behaviour was also tested in a sample of the compound labelled in the cationic side. Samples of the crushed crystals were heated at 150°C and 170°C for 1 hour and 10 minutes, and the results are presented in Table 6.7 where they can be compared both with those for the untreated sample and also with the results for the compound labelled in the anionic side. These results confirm that crushing had no effect on exchange and also that the followed reaction was the same, no matter which site was labelled initially.

6.2 Mathematical treatment of the experimental data

The procedure described in chapter 5, section 5.2, was used to analyse the isochronal and isothermal data obtained from samples A and B of the compound $[Co(NH_3)_5Cl]Cl_2$.

Table 6.5 Isothermal heating of $[Co(NH_3)_5{}^{36}Cl]Cl_2$.

Temperature: 160°C.

Period of heating t (hours)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
1	4.9	95.1
3	10.7 ± 1.2	89.3 ± 1.2
5	11.1	88.9
8	11.6 ± 0.8	88.4 ± 0.8
12	13.0	87.0
21	14.3 ± 0.3	85.7 ± 0.3

Table 6.6 Isothermal heating of $[Co(NH_3)_5Cl]^{36}Cl_2$.

Temperature: 160°C.

Period of heating t (hours)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
1	5.6 ± 0.4	95.2 ± 0.4
3	10.3	89.7
5	11.3 ± 0.7	88.7 ± 0.7
8	12.2	87.8
12	13.9 ± 1.5	86.1 ± 1.5
21	16.5 ± 2.5	83.5 ± 2.5

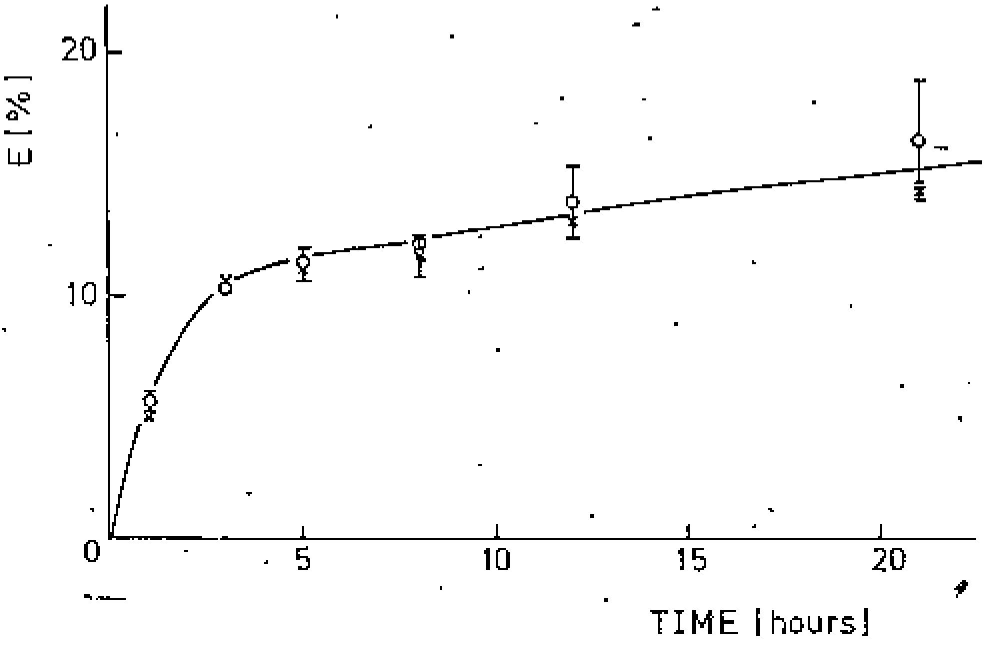

Fig. 6.4 The exchange isothermals at 160°C.

O : $[Co(NH_3)_5Cl]^{36}Cl_2$

X : $[Co(NH_3)_5{}^{36}Cl]Cl_2$

Table 6.7 Exchange measurements on a crushed sample of $[Co(NH_3)_5{}^{36}Cl]Cl_2$. The results for a crushed sample of $[Co(NH_3)_5Cl]^{36}Cl_2$ and for the untreated samples of the compound labelled in the cationic and in the anionic sides are also given for comparison.

		Crushed sample	Untreated sample
Sample	Temperature T (°C)	Percentage of exchange E (%)	Percentage of exchange E (%)
$[Co(NH_3)_5{}^{36}Cl]Cl_2$	150	3.2 ± 1.2	4.2 ± 0.7
	170	6.2 ± 0.5	6.0 ± 0.8
$[Co(NH_3)_5Cl]^{36}Cl_2$	150	3.9 ± 0.8	3.6 ± 0.6
	170	6.7 ± 1.3	5.9 ± 1.2

The results of this analysis are presented in Table 6.8. They show that the most probable number of reaction paths available for the exchange process is from two to three. This is consistent with the shape of the semi-logarithmic plot of Figure 6.5 for the isothermal exchange data which also suggests that more than one reaction path is available.

Figure 6.6 shows the calculated and experimental isochronal curves for samples A and B, and Figure 6.7 the calculated and experimental isothermal curves for sample B.

Table 6.8 The results of the mathematical analysis for Samples A and B of $[Co(NH_3)_5Cl]Cl_2$.

	Sample A (untreated)		Sample B (untreated)					
	Isochronal data		Isochronal data		Isothermal data		Isochronal + isothermal data	
	Energy of activation	Proportion	Energy of activation	Proportion	Energy of activation	Proportion	Energy of activation	Proportion
	E_a (eV)	P (%)	E_a (eV)	P (%)	E_a (eV)	P (%)	E_a (eV)	P (%)
One reaction path	1.681	100.00	1.791	100.00	1.758	100.00	1.768	100.00
Two reaction paths	1.490	8.99	1.552	4.85	1.627	10.61	1.621	10.86
	1.706	91.01	1.818	95.15	1.822	89.39	1.855	89.14
Three reaction paths	1.317	1.74	1.442	1.71			1.448	2.02
	1.508	7.85	1.608	5.45	-	-	1.652	11.57
	1.708	90.41	1.836	92.84			3.097	86.41
Frequency factor V(s^{-1})	1.0×10^{15}		1.0×10^{15}		1.0×10^{15}		1.0×10^{15}	

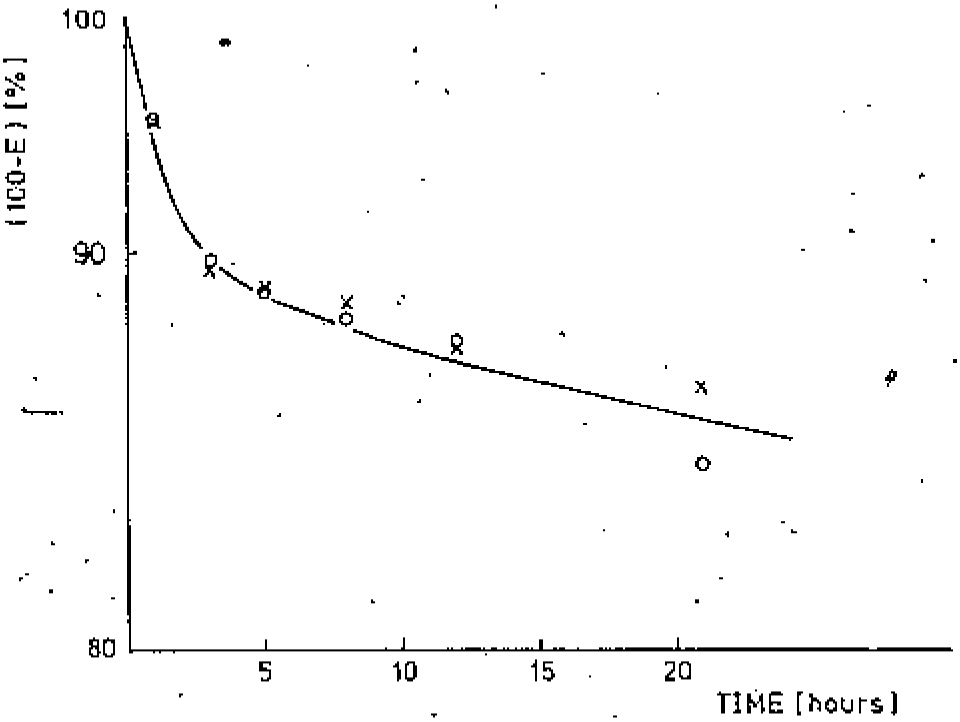

Fig. 6.5 The exchange isothermals of $[Co(NH_3)_5Cl]^{36}Cl_2$ (O) (sample B) and $[Co(NH_3)_5{}^{36}Cl]Cl_2$ (X). Temperature: 160°C

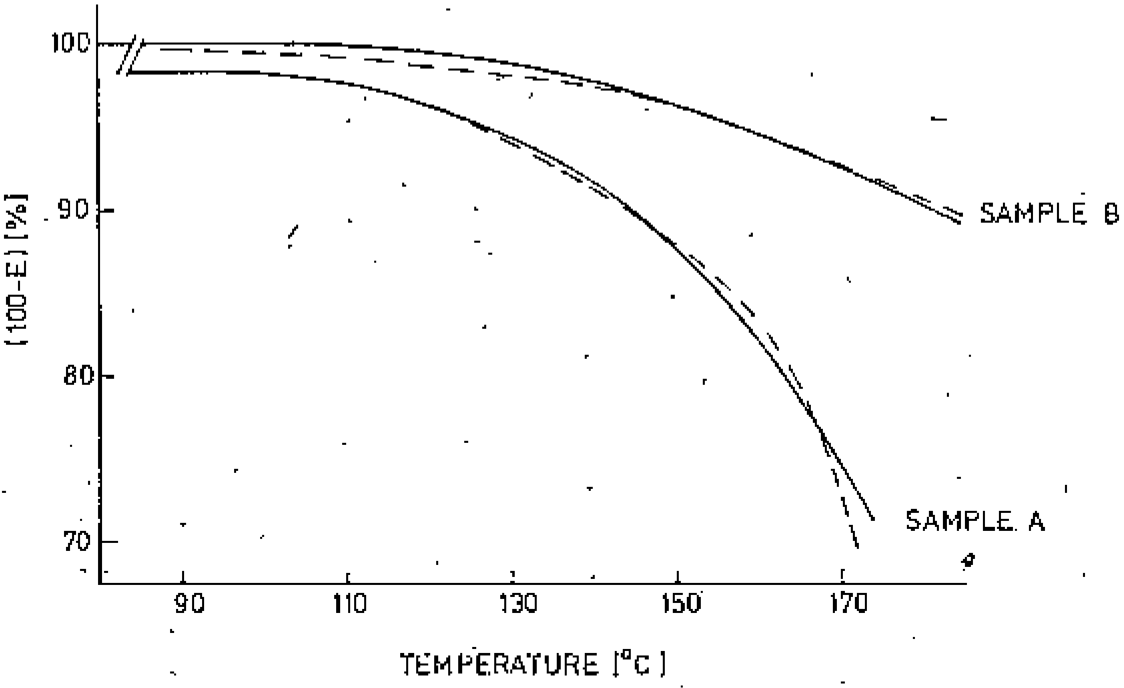

Fig. 6.6 The exchange isochronals of $[Co(NH_3)_5Cl]^{36}Cl_2$.

Samples A and B. Time: 1 h 10 min

Experimental curves: ———

Calculated curves: ------

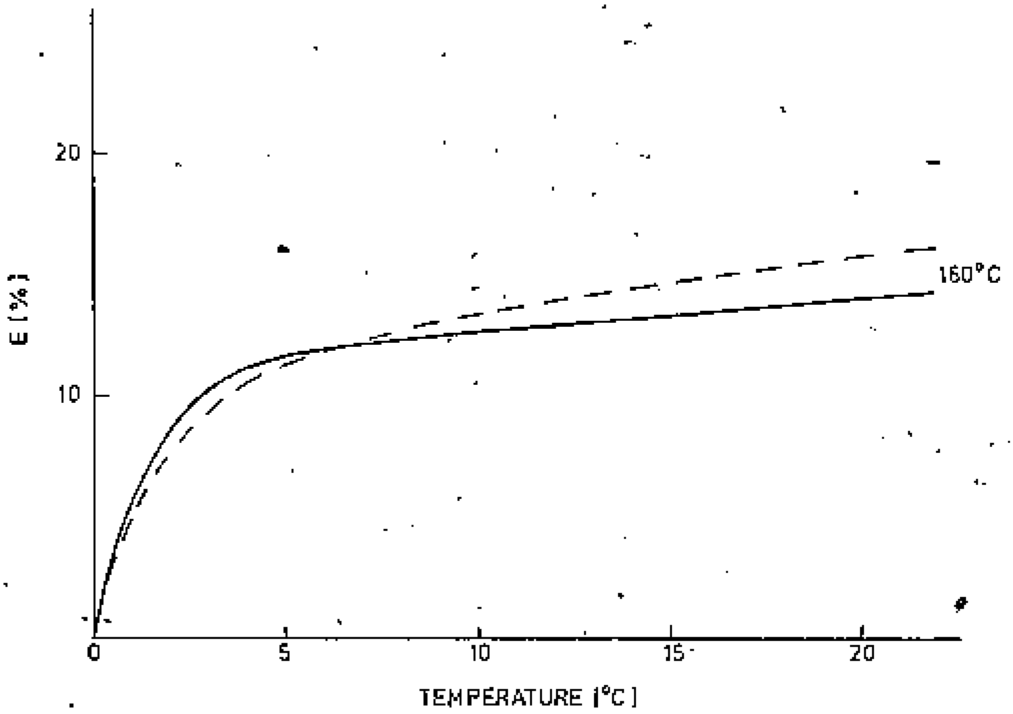

Fig. 6.7 The exchange isothermal of $[Co(NH_3)_5Cl]^{36}Cl_2$.

Sample B. Temperature: 160°C

Experimental curve: ——

Calculated curve: ------

CHAPTER 7 - EXCHANGE STUDIES ON $Cr_2(C_2O_4)_3.6H_2O$ page

CHAPTER 7 - EXCHANGE STUDIES ON $Cr_2(C_2O_4)_3.6H_2O$

This chapter contains the results of the experiments which were performed on the chromium (III) oxalates, $[^{51}Cr(H_2O)_6][Cr(C_2O_4)_3]$ and $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$, to investigate the exchange reactions between the chromium atoms lying in the cationic and anionic sites of the compounds. The data are analysed by the mathematical method described in chapter 5 (based on equation (2.6)) on the assumption of one, two or three reaction paths.

Isochronal measurements were made on both compounds, the period of heating being two hours. Isothermal measurements at several different temperatures were also made on samples of the compound $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$. The experimental results are expressed as percentages of exchange, having been corrected for apparent zero-time exchanges (see chapter 4, section 4.2).

The errors stated are the standard deviations from the mean values when more than one determination was carried out on a given sample.

7.1 Experimental results

7.1-1 Isochronal treatment of $[^{51}Cr(H_2O)_6][Cr(C_2O_4)_3]$

In spite of the fact that decomposition was observed in this compound due to an increase in temperature (see the decomposition analysis, chapter 4, section 4.8-2), isochronal measurements were made on the sample to observe the exchange behaviour. The results are presented in Table 7.1 and Figure 7.1

Table 7.1 Isochronal heating of $[^{51}Cr(H_2O)_6][Cr(C_2O_4)_3]$.

Time: 2 hours.

Temperature T (^{o}C)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
22	1.6	98.4
32	1.8 ± 0.5	98.2 ± 0.5
50	6.8 ± 1.2	93.2 ± 1.2
64	9.3 ± 0.8	90.7 ± 0.8
74	15.8	84.2
90	23.5 ± 2.5	76.5 ± 2.5
100	44.5	55.5
110	92.3	7.7

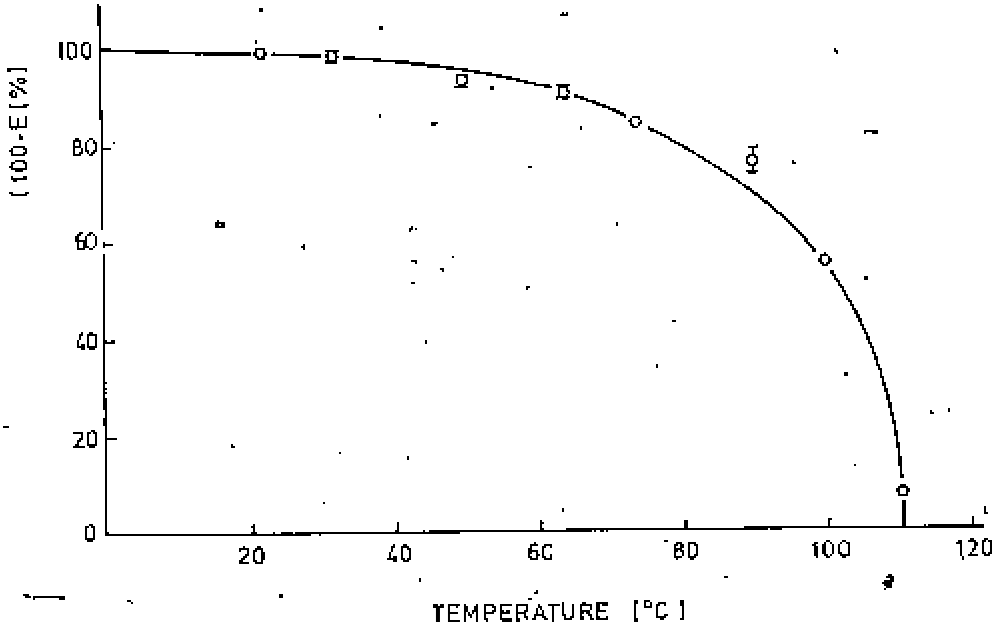

Fig. 7.1 The exchange isochronal of $[^{51}Cr(H_2O)_6][Cr(C_2O_4)_3]$.

Time: 2 hours

7.1-2 Isochronal and isothermal treatments of $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$

The results of the isochronal exchange measurements are shown in Table 7.2 and are plotted in Figure 7.2.

Isothermal measurements were made at temperatures of 30°C, 40°C, 46°C and 60°C, for periods of time ranging from one to eighty hours. These results are shown in Tables 7.3 to 7.6 and are presented graphically in Figure 7.3

Isothermal measurements were also made at room temperature (20°C). The results are shown in Tables 7.7 and in Figure 7.4. It can be seen that even at temperatures as low as room temperature, exchange takes place in this compound.

7.2 Mathematical analysis of the experimental data

The experimental data for the two chromium oxalates were analysed according to the procedure described in chapter 5, section 5.2. The results for both compounds are displayed in Table 7.8.

The best fit to the isochronal data for $[^{51}Cr(H_2O)_6][Cr(C_2O_4)_3]$ was obtained on the assumption of two energies of activation. For the compound $[^{51}Cr(C_2O_4)(H_2O_4][Cr(C_2O_4)_2(H_2O)_2]$, both the isochronal and isothermal data were fitted best on the assumption of three energies of activation. The shapes of the curves in Figure 7.5, which shows a semi-logarithmic plot of the unexchanged fraction against time for the exchange isothermals on $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$, suggest that more than one reaction occurs in the solid.

In Figure 7.6 the calculated and the experimental

Table 7.2 Isochronal heating of $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$. Time: 2 hours.

Temperature T (°C)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
21	0.4	99.6
25	1.2	98.8
27	1.2	98.8
30	4.5	95.5
35	4.0	96.0
40	6.2	93.8
45	9.5 ± 1.8	90.5 ± 1.8
50	11.0 ± 0.4	89.0 ± 0.4
55	15.0	85.0
60	17.5 ± 1.2	82.5 ± 1.2
65	33.4 ± 1.4	66.6 ± 1.4
70	38.9	61.1
75	60.8	39.2
80	71.7 ± 1.4	28.3 ± 1.4
90	78.8	21.2
100	95.1	4.9

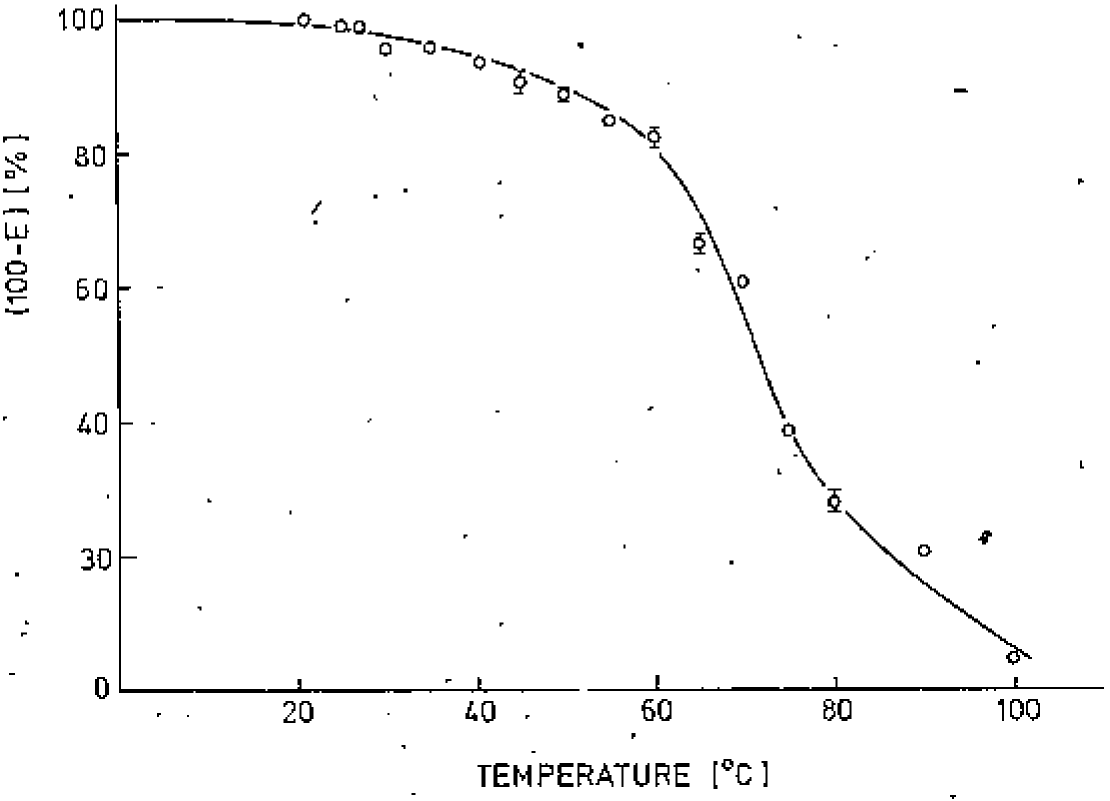

Fig. 7.2 The exchange isochronal of $[^{51}Cr(C_2O_4)(H_2O)_4]$ - $[Cr(C_2O_4)_2(H_2O)_2]$. Time: 2 hours

Table 7.3 Isothermal heating of $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$. Temperature: 30°C.

Period of heating t (hours)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
1	2.2	97.8
2	3.1	96.9
5	2.5	97.5
7	2.8 ± 0.7	97.2 ± 0.7
10	4.6 ± 1.0	95.4 ± 1.0
20	4.2 ± 0.8	95.8 ± 0.8
30	6.2	93.8
40	6.6	93.4
50	7.0	93,0
60	6.5	93.5
72	7.6	92.4

Table 7.4 Isothermal heating of $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$. Temperature: 40°C.

Period of heating t (hours)	Percentage of exchange E (%)	Unexchanged fraction (100-E)(%)
2	5.4	94.6
5	7.1 ± 0.7	92.9 ± 0.7
7	8.0	92.0
10	8.3 ± 1.0	91.7 ± 1.0
20	11.0	89.0
30	14.0 ± 1.2	86.0 ± 1.2
40	14.4	85.6
50	14.0	86.0
60	15.0	85.0
72	15.4	84.6

Table 7.5 Isothermal heating of $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$. Temperature: 46°C.

Period of heating t (hours)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
1	5.7	94.3
2	6.1	93.9
5	8.9	91.1
7	9.0 ± 1.0	91.0 ± 1.0
20	13.7 ± 1.2	86.3 ± 1.2
30	17.0	83.0
40	18.2	81.8
50	20.1	79.9
60	22.1	77.9
72	21.7	78.3

Table 7.6 Isothermal heating of $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$. Temperature: 60°C.

Period of heating t (hours)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
1	8.1	91.9
5	14.8 ± 1.4	85.2 ± 1.4
10	21.8 ± 1.2	78.2 ± 1.2
20	23.7 ± 1.8	76.3 ± 1.8
30	26.9	73.1
50	29.5	70.5
57	30.2	69.8
70	34.0	66.0
80	32.8	67.2

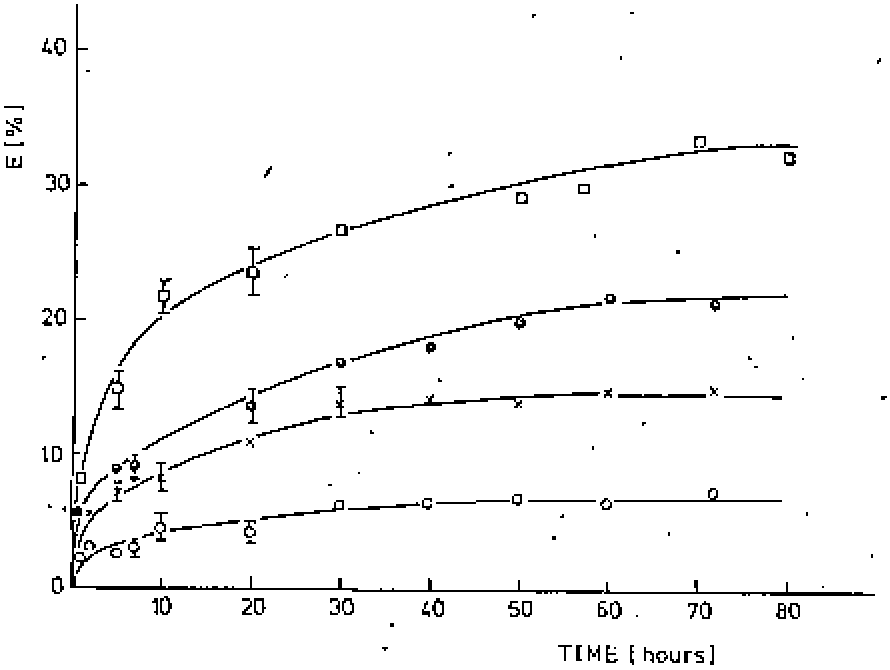

Fig. 7.3 The exchange isothermals of $[^{51}Cr(C_2O_4)(H_2O)_4]$ $[Cr(C_2O_4)_2\ (H_2O)_2]$.

O : 30°C ; X : 40°C ; ● : 46°C ; □ : 60°C

Table 7.7 Isothermal heating of $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$. Temperature: ~ 20°C (room temperature).

Period of heating t (days)	Percentage of exchange E (%)	Unexchanged fraction (100-E) (%)
1.2	6.0 ± 0.5	94.0 ± 0.5
5.1	13.6 ± 1.1	86.4 ± 1.1
20.1	23.6	76.4
33.2	25.4 ± 0.5	74.6 ± 0.5
45.2	25.7	74.3

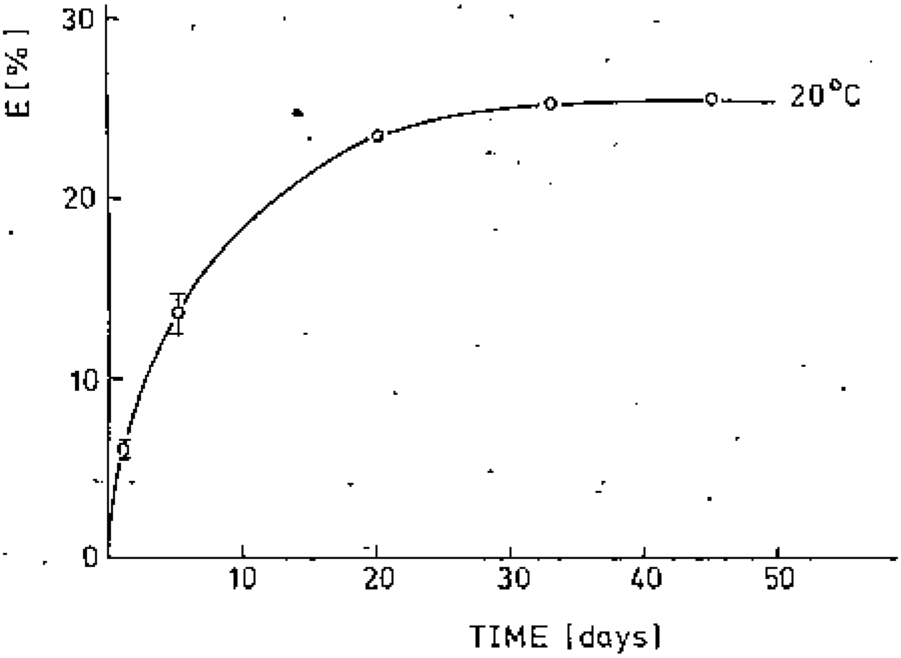

Fig. 7.4 The exchange isothermal of [$^{51}Cr(C_2O_4)(H_2O)_4$] [$Cr(C_2O_4)_2(H_2O)_2$]. Temperature : ~ 20°C (room temperature)

Table 7.8 The results of the mathematical analysis for the compounds $[^{51}Cr(H_2O)_6][Cr(C_2O_4)_3]$ and $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$.

	$[Cr(H_2O)_6][Cr(C_2O_4)_3]$		$[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$					
	Isochronal data		Isochronal data		Isothermal data		Isochronal + isothermal data	
	Energy of activation	Proportion	Energy of activation	Proportion	Energy of activation	Proportion	Energy of activation	Proportion
	E_a (eV)	P (%)	E_a (eV)	P (%)	E_a (eV)	P (%)	E_a (eV)	P (%)
One reaction path	1.093	100.00	1.287	100.00	1.352	100.00	1.458	100.00
Two reaction paths	0.921	7.46	1.200	15.62	1.215	16.05	1.330	19.18
	1.098	92.54	1.305	84.38	1.379	83.95	1.482	80.82
Three reaction paths			1.146	7.35	1.163	5.52	1.290	8.60
	–	–	1.278	64.19	1.255	15.47	1.394	23.67
			1.371	28.46	1.391	79.01	1.497	67.73
Frequency factor $\nu(s^{-1})$	5.0×10^{10}		5.0×10^{14}		5.0×10^{14}		3.5×10^{16}	

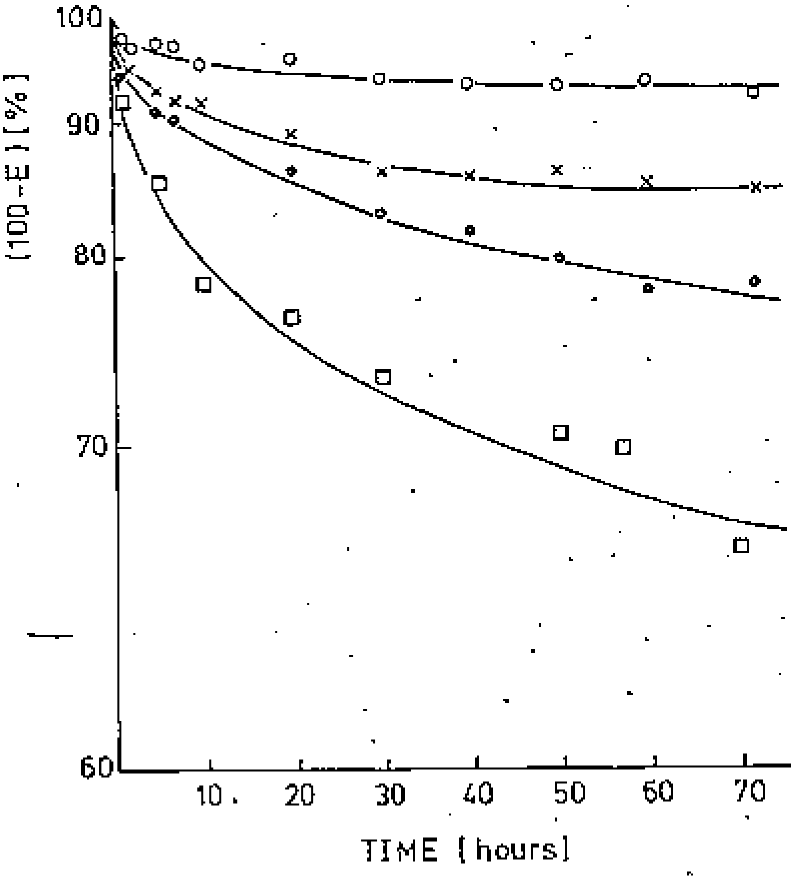

Fig. 7.5 The exchange isothermals of

$[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2\ (H_2O)_2]$

○ : 30°C ; X : 40°C ; ● : 46°C ; □ : 60°C

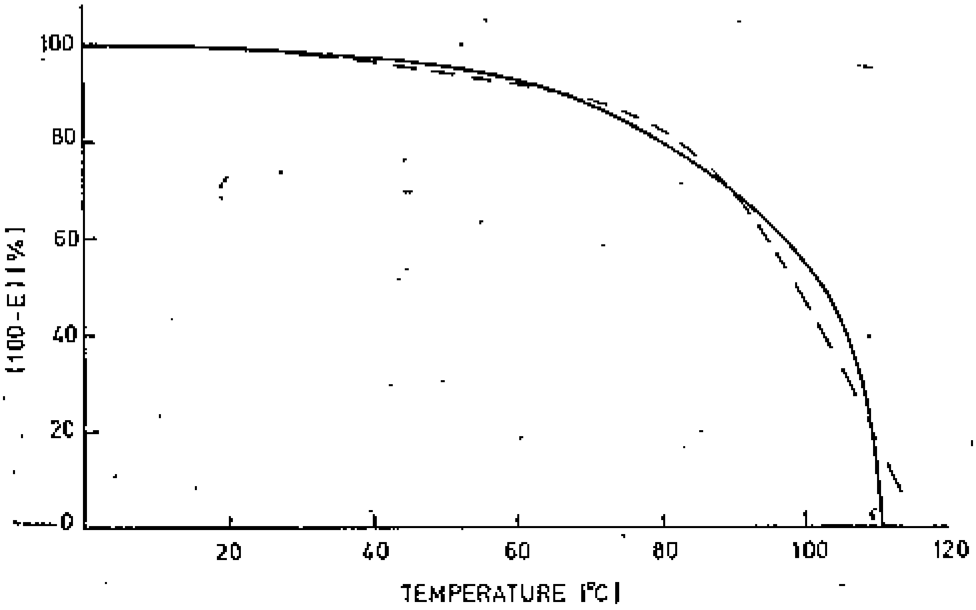

Fig. 7.6 The exchange isochronal of $[^{51}Cr(H_2O)_6][Cr(C_2O_4)_3]$. Time: 2 hours

Experimental curve: ———

Calculated curve: ------

isochronals for $[^{51}Cr(H_2O)_6][Cr(C_2O_4)_3]$ are compared. Figure 7.7 shows the calculated and experimental isochronal curves for the compound $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$. Figure 7.8 shows the calculated and experimental isothermal curves for this compound.

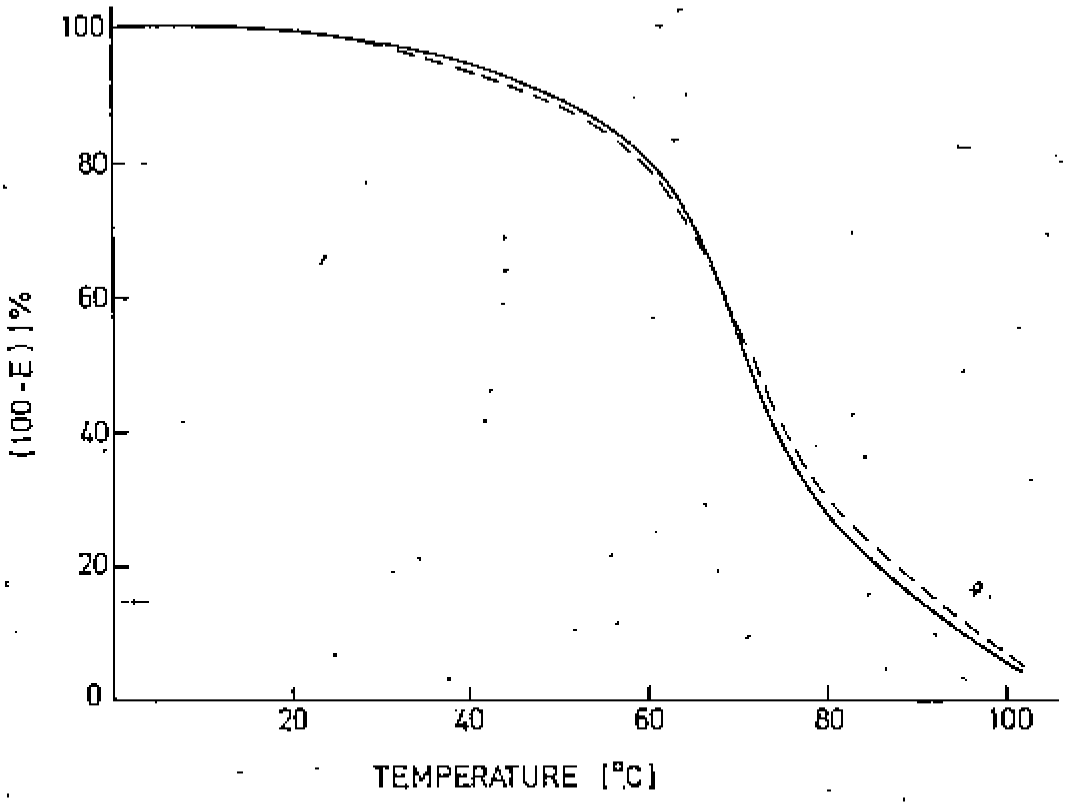

Fig. 7.7 The exchange isochronal of

$[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$. Time: 2 hours

Experimental curve: ———

Calculated curve: ------

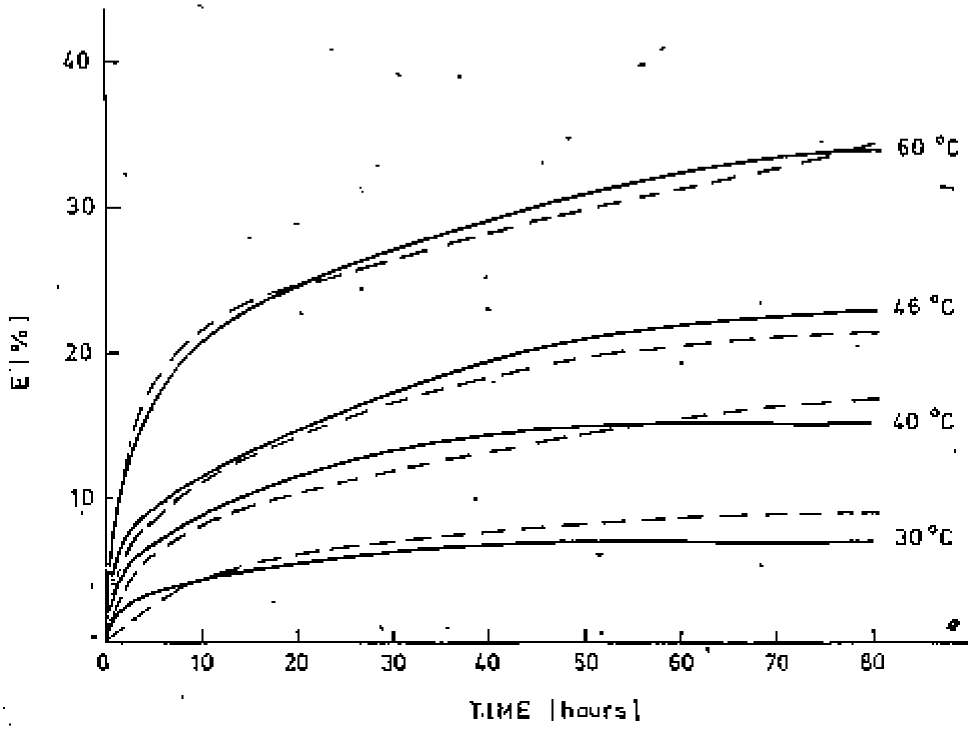

Fig. 7.8 The exchange isothermals of

$[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$

Experimental curves: ———

Calculated curves: ------

CHAPTER 8 - DISCUSSION AND CONCLUSIONS page

CHAPTER 8 – DISCUSSION AND CONCLUSIONS

8.1 Discussion of results

8.1-1 $[Fe\ (H_2O)_6][Fe\ EDTA\ (H_2O)]_3.H_2O$.

Our experiments have shown that exchange between the iron atoms in the compound $[Fe\ (H_2O)_6][Fe\ EDTA\ (H_2O)]_3.H_2O$ can be followed in the temperature range 100 to 150°C, at which temperature decomposition becomes serious (see decomposition analysis, chapter 4, section 4.6-2).

It was observed that different preparations of the compound gave different exchange isochronals; the curves may be compared in Figure 5.1, chapter 5. These differences, which have already been observed by other workers (Fernandez Valverde _et al._ 1978, Nyarku 1978), can be attributed to the density of defects, which may vary from one preparation to another.

The influence of the method of preparation on the exchange processes may also be seen in the mathematical analysis of samples A and B (Table 5.9; chapter 5). The analysis applied to the set of isochronal data gave a better fit with two energies of activation for sample A while three seemed better for sample B. The values of the energies of activation and of the proportions of the reactions were (from Table 5.9):

Sample A		Sample B		
E_a (eV)	P (%)	E_a (eV)	P (%)	
		1.532	1.47	42.24
1.655	50.22	1.678	40.77	
2.941	49.78	2.850	57.76	

It can be seen that the first reaction in sample B is hardly distinguishable from the second one. We can suppose that the exchange data can be characterised with two energies of activation.

Before we proceed on this discussion it should be mentioned that we are dealing only with a very limited set of isochronal data from which we must determine a great many parameters. Because of this there is some uncertainty in the values of the higher energies of activation. This difficulty was relieved for sample B by incorporating isothermal data with the isochronal data. The value of the higher energy of activation was thus determined more precisely; its value was 2.928 eV.

Considering that the value 2.928 eV was the energy of the second main reaction in both samples A and B, and assuming that the energies of the first main reactions were the same in both samples, it appears that the method of preparation mostly affected the proportions of the two reactions. In sample A there was an increase in the proportion exchanging by the low-activation-energy process. It is most likely that a higher defect density in sample A favoured the exchange by this path.

The analysis of the isothermal data for sample B gave a better fit with two energies of activation, showing no improvement in the fitting with three energies of activation. The analysis of the isochronal plus isothermal data gave a better fit with three energies of activation.

The concordance between the individual values of the energies and proportions of the different reactions between one set of data and another is not so good, but this does not prevent us reaching useful conclusions. From the results shown in Table 5.9, chapter

5, it appears that the data are better fitted supposing the existence of three different processes but that two energies of activation are enough to characterise the main processes.

Now, if we look at the experimental isochronal curve for sample B (shown in Figure 5.1, chapter 5) we can see that three successive exchange processes occur as the temperature is raised. The sloping portions of the curve that define regions of temperature where exchange occurs at a measurable rate, give us an insight into the sort of processes that might have induced exchange.

The sloping portion of the curve above 140°C can be related to decomposition. It has already been observed that exchange happens simultaneously with the thermal decomposition (Lazzarini & Lazzarini 1976). Some complexes, however, also show exchange in a narrow range of temperature just below the temperature of decomposition. The second sloping portion of the isochronal curve for sample B is situated in such a region, and it suggests that an exchange process is somehow correlated with the process of decomposition.

We propose the following model to account for such a correlation:

Consider the process of decomposition of a complex anion A^- giving cations X^{n+}, and ligands Y^{n-}, according to:

$$A^- \underset{}{\overset{\text{fast}}{\rightleftharpoons}} X^{n+} + Y^{n-} \xrightarrow{\text{slow}} \text{irreversible products}$$

In the reversible equilibrium represented by the first stage of the above process the products do not separate but remain in the unit cell. Only a small fraction proceed to the irreversible decomposition step. But it can be also considered that at low temperatures part of the ligands and cations can recombine again frequently, this stage of the process being reversible. Because this reversible reaction within the unit cell may incorporate the other cationic species it may lead to exchange.

Consider now the rate of these processes, $k = \nu e^{-E_a/kT}$; if we suppose that the frequency factor is higher for exchange than for decomposition ($\nu_E > \nu_D$) and that the energies of activation, E_a, are the same for both processes, then exchange will take place at a slightly lower temperature than decomposition. This provides an explanation for the exchange reaction observed in a narrow range of temperature just below the temperature where decomposition is observed.

The traditional methods of analysing the data (i.e. supposing the energy for exchange is lower than for decomposition, and that the frequency factors are the same, $\nu_E = \nu_D$) do not provide a satisfactory explanation for what is observed experimentally. Examining again the results of the mathematical analysis shown in Table 5.9, chapter 5, which was made with these assumptions, it can be seen that the calculated energy of activation for the third process seems to be too high compared with the energies of the two first processes. We must doubt, with Maddock (1975a), that the assumption ν = constant, is not always valid.

The first sloping region of the isochronal curve for sample B (Figure 5.1, chapter 5) suggests that an exchange process may be related to the dehydration of the compound. It is well-known that the processes of hydration and dehydration can induce either annealing or exchange (Lazzarini & Fantola-Lazzarini 1975, 1976, Bolton & McCallum 1957; Shankar et al. 1965). We tested this by performing experiments with a sample of the compound that was dehydrated before the isochronal treatment. The results obtained in this case can be compared with those for the untreated sample (hydrated) in Table 5.7, chapter 5; it can be seen that there is more exchange in the hydrated sample than in the dehydrated one. It seems that dehydration converted the crystalline lattice into a more densely packed system where exchange could only take place with greater difficulty.

An interesting result was obtained when hydrated samples were heated in opened ampoules (Figure 5.6, chapter 5). The isochronal curve so obtained overlaps the one for the dehydrated sample. This suggests that the dehydration by itself was not responsible for the exchange observed. However, we can explain the process as follows: when hydrated samples were heated in sealed ampoules, the water liberated by dehydration was not allowed to escape, and could easily be reabsorbed by the hygroscopic product. Thus, successive processes of hydration and dehydration could take place during the period of heating, so that there was a continuous restructuring of the crystalline lattice, making the movement of defects or atoms easier, and so inducing the exchange reaction.

The results of the mathematical analysis applied to the set of data for the dehydrated sample, shown in Table 5.10, chapter 5, confirm that the dehydration altered the characteristics of the exchange process. The analysis gave a better fit with two energies of activation, showing no improvement on the fitting with three energies of activation. The results were:

E_a (eV)	P (%)
1.569	1.73
1.771	98.27.

It can be seen that the first reaction is hardly separated from the second one, indicating that exchange in the dehydrated sample is mainly a result of one process, while in the hydrated sample the exchange process is better characterised with two or three energies of activation.

The effect of defects on the exchange reaction was also investigated; their influence can be seen by comparing the isochronals for the untreated sample, for a sample that was gamma-irradiated to a total dose of 5 Mrads, and for a sample that was ground before heating. These isochronal curves are shown respectively in Figures 5.3 and 5.4, chapter 5. It can be observed that the isochronal for the irradiated sample overlaps that for the untreated sample, indicating that ionising irradiation had no appreciable effect upon exchange. By contrast, however, the effect of grinding was very marked (Figure 5.4). Note that the sloping portions of the curve for the crushed sample were shifted to regions of lower temperature. As the temperature at the step reflects the energy of activation we can expect lower energies of activation than in the untreated sample.

The results of the mathematical analysis of the set of isochronal data for the crushed sample, shown in Table 5.11, confirmed this conclusion. The analysis gave a better fit with three energies of activation and the energies of the three processes were lower. There was also some alteration in the proportions of the process, but one still observed a lower proportion exchanging by the low activation energy process and a higher proportion exchanging by the highest energy rate. Hence we must agree with Harbottle and Sutin (1959) that the presence of defects facilitates exchange in the solid lowering the energies of activation necessary for such processes.

Since point defects that must have been introduced by the ionising irradiation had no effect upon exchange, the observed effect of crushing seems to be caused by an enhancement in the dislocation density and, perhaps, greater surface area of the ground material. It is known already that dislocations play an important role in many solid-state reactions. For example, it is to be expected that diffusion or migration will proceed more rapidly along a dislocation line than through an undisturbed part of the crystal. A dislocation can also act as a sink or source of vacancies. Generally, one may expect that in equilibrium the density of vacancies will be greater in the vicinity of a dislocation than in the rest of the lattice (Billington & Crawford 1961).

All these facts suggest that the exchange process involved migration of atoms and/or vacancies within the solid, the reaction occurring in the disordered regions of the crystal. These movements were helped by successive processes of hydration and dehydration of the sample.

The following conclusions can be drawn from the exchange studies on the compound $[Fe\ (H_2O)_6][Fe\ EDTA\ (H_2O)]_3.H_2O$:

(i) The solid-state exchange reaction may be interpreted using a model which assumes that the whole exchange process is the result of first-order reactions showing a spectrum of energies of activation.

(ii) The exchange process observed in this particular system appears to be the result of three reactions.

(iii) There is some experimental evidence to suggest that there are changes in the frequency factor, υ, during the heating.

(iv) Different preparations of the compound can lead to different results: the proportions of the exchange proceeding by the different paths varied from preparation to preparation.

(v) γ-irradiation, which introduces point-defects in the solid, does not promote exchange and failed to facilitate subsequent thermal exchange.

(vi) The crushing of crystals, which increased the dislocation density in the solid, did affect the subsequent thermal exchange process, altering the energies of activation and the proportions exchanging by the different pathways.

(vii) Dehydration of the compound alters the pathways for the process, making exchange more difficult while hydration makes it easier.

(viii) The exchange appears to involve movement of atoms and/or vacancies within the solid, the reaction occurring in the disordered regions of the crystal.

8.1-2 $[Co(NH_3)_5Cl]Cl_2$

Experiments performed with sample B of the compound $[Co(NH_3)_5Cl]^{36}Cl_2$ (prepared by precipitation from solution) showed that exchange between the complex-bound Cl atoms and ionic chlorine was relatively small in the range 100-180°C (Table 6.3, chapter 6).

Measurements made on sample A (prepared by complete freeze-drying of a solution of $[Co(NH_3)_5Cl]^{36}Cl_2$; see chapter 3, section 3.5-2) gave higher values for the percentages of exchange. Figure 6.2, chapter 6, shows the isochronal curves for both preparations where it can be seen that the differences between the two samples were greater than the experimental errors.

The results of the mathematical analysis applied to the set of isochronal data for samples A and B (Table 6.8, chapter 6) confirm the experimental evidence that the two different preparations led to different parameters for exchange. The analyses gave the best fit with three energies of activation for both samples. Although the values of the energies of activation changed from one sample to another their spacings, in eV, appeared constant. The proportions of the processes in both samples were substantially the same.

Analysis of the isothermal data for sample B gave the best fit with two energies of activation.

The results of the analysis of the isochronal and the isothermal data for sample B are reproduced here (taken from Table 6.8):

Isochronal data			Isothermal data	
E_a (eV)	P (%)		E_a (eV)	P (%)
1.442	1.71	7.16		
1.608	5.45		1.627	10.61
1.836	92.84		1.822	89.39

It can be seen that the proportion exchanging by the lower energy route is very low, 1.71%, indicating that this first process is of little importance. If we assume, then, that there are two main processes occurring in the solid, we can see that the values of the energies of activation and of the proportions of the reactions for both sets of data agree well.

The analysis of the set of isochronal plus isothermal data gave a better fit with three energies of activation. These results (Table 6.8, chapter 6) also show a low proportion, 2.02%, exchanging by the lower energy-of-activation-path, which agrees with the analysis of the isochronal data taken alone. The analysis of the isothermal data alone did not give this result, but the set of isothermal data may have been too small to calculate so many parameters accurately.

Comparing now the energies of activation for the isochronal and isochronal plus isothermal sets of data, we can see that there is good agreement in their values for the two first reactions. The third values disagree, however. These may be influenced by the data for long exchange times: after long periods of heating the reaction proceeds very slowly so that even the best value of ν does not give a complete overlap of isothermals at different temperatures when plotted as E% vs ln t. This indicates that there are also changes in the frequency factor, ν, accompanying the distribution of energies of activation (Maddock 1975a).

The experiments made to investigate the influence of defects on the solid-state exchange reaction showed that treatments like crushing and gamma-irradiation had no effect upon this exchange. It can be seen from Figure 6.3, chapter 6, that the isochronal curve for the crushed sample overlaps that for the untreated sample. This indicates that dislocations, and an increase in the surface area created by crushing the crystals, did not affect the exchange reaction. The failure of γ-irradiation to induce exchange and to promote the subsequent thermal exchange indicates that point defects do not affect the exchange either. Figure 6.1 shows the isochronals for the irradiated and the untreated samples overlapping each other.

The solid-state exchange reaction could be a result of loss of ammonia leading to the formation of tetramminecobalt (III) chloride according to:

$$[\mathrm{Co\ (NH_3)_5\ Cl}]{}^{36}\mathrm{Cl_2} \rightarrow [\mathrm{Co\ (NH_3)_4}{}^{36}\mathrm{Cl_2}]\mathrm{Cl} + \mathrm{NH_3}\ .$$

This possibility was investigated by measuring the exchange in a sample of the compound labelled in the cationic side. The overlap of the exchange isothermals for samples of the compound labelled in the cationic and in the anionic sides (shown in Figure 6.4, chapter 6) gave evidence that a true exchange reaction was involved. This was confirmed by the fact that a crushed sample of $[\mathrm{Co\ (NH_3)_5}{}^{36}\mathrm{Cl}]\mathrm{Cl_2}$ showed the same exchange behaviour as a crushed sample of the compound labelled in the ionic chlorine. These results are shown in Table 6.7, chapter 6.

Since solid-state exchange was not affected by the defects created by ionising radiation or by crushing the crystals, and since it was not a result of decomposition, it appears that the reaction must have proceeded via ligand vacancies. Such a mechanism was proposed by Bell and collaborators (1972) to account for the solid-state exchange reaction in hexahalo complexes of

Re (IV), and it is formulated as follows:

1. Ligand-vacancy formation:

$$[Co\ (NH_3)_5\ Cl]^{2+} \rightleftharpoons [Co\ (NH_3)_5\ \square\ ]^{3+} + Cl^-$$

2. Ligand-vacancy migration:

$$[Co\ (NH_3)_5\ Cl]^{2+} + [Co'\ (NH_3)_5\ \square\ ]^{3+} \rightleftharpoons [Co\ (NH_3)_5\square\ ]^{3+} + [Co'\ (NH_3)_5\ Cl]^{2+}$$

3. Nucleophilic substitution by radiohalide:

$$[Co\ (NH_3)_5\ \square\ ]^{3+} + {}^{36}Cl \rightarrow [Co\ (NH_3)_5\ {}^{36}Cl]^{2+}\ .$$

According to this mechanism, ligand vacancies present after preparation of the compound or formed by thermal treatment may interact with the nearest ligands of the neighbouring molecules if sufficient vibrational energy is available. This leads to the migration of the vacancies which will then be filled when moving close to dopant ions.

The difference between this mechanism and the customary solid-state transport mechanism is that ligand-vacancy migration involves only an individual part of the anion instead of the complete lattice constituent.

The following conclusions can be drawn from the analysis of the experimental exchange data on the compound $[Co\ (NH_3)_5\ Cl]Cl_2$:

(i) The experimental data may be characterised by a model which assumes the exchange process to be a result of first-order reactions with distributed energies of activation.

(ii) The transfer of activity within the solid appears to be the result of three different processes.

(iii) The analysis of the data suggests that there are also changes in the frequency factor, ν, and not only in the energies of activation on heating.

(iv) Different preparations can lead to different results: the energies of activation of the processes occurring in two samples prepared by two different methods differed between one sample and the other.

(v) Pre-treatments of the sample by γ-irradiation and crushing failed to induce exchange or to enhance the subsequent thermal exchange process.

(vi) The exchange reaction appears to proceed via ligand-vacancy migration.

8.1-3 $Cr_2(C_2O_4)_3.6H_2O$

The mathematical analysis applied to the isochronal data obtained for the compound $[^{51}Cr(H_2O)_6][Cr(C_2O_4)_3]$ gave a better fit with two energies of activation, as shown in Table 7.8, chapter 7, where the results of the analysis applied to the isochronal, isothermal and isochronal plus isothermal data for the compound $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$ are also shown. The analysis gave better fits with three energies of activation for the three sets of data.

Comparing the values of the energies of activation obtained from the analysis of the isochronal and the isothermal data, we can see that there is good agreement between them. The analysis of the isochronal plus isothermal data however gave a larger value of ν and larger values of the energies of activation; nevertheless their spacing, in eV, is substantially the same.

It should be mentioned that, although we assumed a constant value of $\upsilon = 3.5 \times 10^{16}$ when fitting the isochronal plus isothermal data, we did in fact observe that a better fitting was obtained as higher values of υ were assumed, suggesting that υ was actually larger. A frequency factor as high as 10^{18} s^{-1} was reported by Fernandez Valverde <u>et al</u>. (1978). Odru and Vargas (1971) found that their data on annealing of copper phtalocyanine could only be fitted when very high frequency factors were assumed.

Such high frequency factors are mainly a consequence of the data for long times of isothermal heating, since these results are liable to larger errors than the data obtained for short heating periods. It has also been observed that isothermal data can be fitted better with a combination of a high frequency factor and higher energy-of-activation values (Fernandez Valverde <u>et al</u>. 1978). It is difficult to believe in the reality of such high values of υ .

Comparing now the proportions of the exchange proceeding by the different energy-of-activation paths, it can be seen that under isochronal heating a higher proportion exchanges by the second energy-of-activation route, and under isothermal heating a higher proportion exchanges by the higher energy-of-activation route. This last result applied to the set of isochronal plus isothermal data as well. We conclude that on heating, not only the energies of activation, E_a, or the frequency factors, υ , but also the distribution function, $F'(E_a)$, might vary.

The experiments with the chromium (III) oxalates showed that heating induces the decomposition of $[Cr\ (H_2O)_6][Cr\ (C_2O_4)_3]$ into $[Cr\ (C_2O_4)(H_2O)_4][Cr\ (C_2O_4)_2.(H_2O)_2]$ and that this decomposes further on heating with the formation of $[Cr\ (C_2O_4)_3]^{3-}$ (see decomposition analysis, chapter 4, section 4.8-2). We also observed that this thermal decomposition was accompanied by an exchange reaction with the formation of the labelled anions $[^{51}Cr\ (C_2O_4)_2(H_2O)_2]^-$ and $[^{51}Cr\ (C_2O_4)_3]^{3-}$.

Kishore and Venkateswarlu (1971), in their study of the thermal annealing and solid-state isotopic exchange of ^{51}Cr in potassium trisoxalatochromate (III) trihydrate, observed also the presence of ligand-deficient intermediate species such as the unipositive and uninegative chromium (III) oxalato species; they proposed a stepwise mechanism for the conversion of Cr^{3+} to $[Cr\ (C_2O_4)_3]^{3-}$, to explain both the annealing and the exchange reactions. Such a mechanism accounts also for the solid-state exchange reaction observed in the compounds $[^{51}Cr\ (H_2O)_6][Cr\ (C_2O_4)_3]$ and $[^{51}Cr\ (C_2O_4)(H_2O)_4][Cr\ (C_2O_4)_2(H_2O)_2]$, where the exchanging species are present in macroscopic concentrations. The mechanism proposed is expressed by the following sequence of reactions:

$$Cr(H_2O)_6^{3+} + C_2O_4^{2-} \longrightarrow [Cr(C_2O_4)(H_2O)_4]^+ + 2H_2O \qquad (1)$$

$$[Cr(C_2O_4)(H_2O)_4]^+ + C_2O_4^{2-} \longrightarrow [Cr(C_2O_4)_2(H_2O)_2]^- + 2H_2O \qquad (2)$$

$$[Cr(C_2O_4)_2(H_2O)_2]^- + C_2O_4^{2-} \longrightarrow [Cr(C_2O_4)_3]^{3-} + 2H_2O \qquad (3)$$

In the experiments with the compound $[^{51}Cr(H_2O)_6][Cr(C_2O_4)_3]$ the unipositive species $[Cr(C_2O_4)(H_2O)_4]^+$ was detected even at low temperatures, while by 110°C reaction (1) was almost complete.

As the temperature increased the unipositive species was converted into $[Cr(C_2O_4)_2(H_2O)_2]^-$; according to reaction (2). The uninegative species was the more stable but at higher temperatures it was converted into $[Cr(C_2O_4)_3]^{3-}$ according to reaction (3).

The last two reactions, (2) and (3), account for the exchange observed in the compound $[^{51}Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$.

The following conclusions can be drawn from the exchange studies on the compounds $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ and $[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$:

(i) The solid-state exchange data can be fitted by a model which assumes that the exchange process is a result of first-order reactions with distributed energies of activation.

(ii) The exchange process observed in the chromium (III) oxalates, $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ and $[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$, is the result of two and three distinct reactions, respectively.

(iii) The analysis of the data gave some evidence that the frequency factor, ν, and the distribution function, $F'(E_a)$, might vary upon heating.

(iv) Exchange is promoted by decomposition involving a stepwise transfer of ligands.

8.2 General conclusions

The experiments showed that not all systems are suitable for exchange studies. Some of the compounds selected for investigation had to be discarded for several reasons, such as rapid exchange during the synthesis-separation stages as was observed in the compound Hg[Hg EDTA]$.xH_2O$, or because of failure to induce exchange by different treatments given to the sample as happened in the compounds Fe[Fe $(CN)_5$ NO]$.xH_2O$ and K Fe[Fe $(CN)_6$]$.xH_2O$. Systems such as the mixed-valence double salts of gold containing $[Au(III)Cl_4]^-$ and $[Au(I)Cl_2]^-$ (Robin & Day 1967), were previously discarded because of the report of fast exchange in solution (Turco & Sordillo 1955b).

The experimental data gave evidence of solid-state isotopic exchange reactions occurring in the compounds $[Fe(H_2O)_6][Fe\ EDTA(H_2O)]_3.H_2O$, $[Co(NH_3)_5Cl]Cl_2$ and in the chromium (III) oxalates $[Cr(H_2O)_6][Cr(C_2O_4)_3]$ and $[Cr(C_2O_4)(H_2O)_4][Cr(C_2O_4)_2(H_2O)_2]$, where the exchanging species occupied two different lattice sites and had the same oxidation state. In these systems the exchanging species were either ions on ordinary lattice sites and complex metal ions as in the compounds $[Fe(H_2O)_6][Fe\ EDTA(H_2O)]_3.H_2O$ and $Cr_2(C_2O_4)_3.6H_2O$, or ligands and outer-anions as in the compound $[Co(NH_3)_5Cl]Cl_2$. Exchanges have already been reported in mixed-valence systems (Fernandez Valverde <u>et al</u>. 1978, Nyarku 1978) and in compounds where the exchanging atom occupied two different lattice sites and had different oxidation states (Lazzarini & Fantola-Lazzarini 1975, 1976).

The mechanisms proposed to explain exchange taking place in the solid-state seem to vary with the system studied. The effects of the treatments applied to the samples also vary from system to system (e.g. Lazzarini & Fantola-Lazzarini 1975, 1976; Fernandez Valverde <u>et al</u>. 1978). Crushing the crystals increased the fraction able to exchange by the lower energy of activation route in the compound $Tl(I)_3.Tl(III)Cl_6$ without changing the energies of activation (Fernandez Valverde et al. 1978), while the same treatment lowered the energies of activation of the different pathways in the compound $[Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3 \cdot H_2O$, and slightly altered the proportions of the different reactions. Since exchange was enhanced in these two systems by crushing the crystals, it appears that the reaction took place only in the disordered regions of the crystal. This is supported by the observation that dehydration converted the compound $[Fe(H_2O)_6]$ $[Fe\ EDTA\ (H_2O)]_3 \cdot H_2O$ into a more densely packed and uniform system where exchange hardly took place (and proceeded by practically only one pathway).

The migration of vacancies, proposed as a mechanism to explain exchange in the compound $[Co(NH_3)_5Cl]Cl_2$, appears to have taken place throughout the whole solid and not only in disordered regions, since crushing the crystals did not affect the exchange (sample B). However, the fact that in another preparation of the compound (sample A), the rate of exchange was higher and the energies of activation of the different pathways were lower than in sample B, suggests that the density of defects was higher in sample A and that this promoted the migration and perhaps creation of vacancies.

In spite of the differences in exchange behaviour observed from compound to compound, it is possible to formulate some general conclusions drawn from what seems to be common behaviour:

(i) The solid-state isotopic exchange between two normal lattice species is well-described by a model which assumes a set of first-order processes with a spectrum of energies of activation. There are some data suggesting that changes in the frequency factor, υ , and perhaps in the distribution function, F'(Ea), are also necessary to fit the experimental data accurately.

(ii) γ-irradiation, crushing and other treatments may favour exchange and alter the energies of activation and/or the proportions of the exchanges proceeding by the different paths.

(iii) Processes of hydration, dehydration and decomposition can influence the exchange.

These characteristics are also common to exchange in "doped systems" and to annealing reactions following nuclear transformations in solids.

As far as further work is concerned it would be interesting to investigate the effect of crushing on a dehydrated sample of $[Fe(H_2O)_6][Fe\ EDTA\ (H_2O)]_3.H_2O$, since it was observed that in this compound the exchange reaction was favoured not only by crushing but also by the successive processes of hydration of the sample; such an experiment may provide a way to observe the effect of crushing alone upon exchange. Further, in view of the fact that the dehydrated sample is a closer-packed system, this experiment would also provide a way to find out whether crushing would be as effective as it was for the untreated sample (hydrated) of the compound.

The use of Mössbauer spectroscopy to observe exchange between normal lattice species has yet to be made. Systems like $Sn[Sn\ EDTA]$ with the complex showing a reasonably high stability constant (K = 18.3; Bottari et al. 1968), and other iron systems such as $[Fe\ (phen)_3](FeCl_4)_2$ or $[Fe\ (dipy)_3](Fe\ Cl_4)_2$, seem to be likely candidates.

More studies involving mixed-valence compounds and double complexes are necessary. A suitable mixed-valence system may be $H_4Cr_2(III)Cr(VI)O_8$ where the two kinds of chromium atoms can be separated with less than 1% exchange (Aten <u>et al</u>. 1953). Double-complexes containing $[Zn\ EDTA]^{2-}$ having a reasonably high stability constant (K = 16.3; Anderegg 1964), or $[Co(C_2O_4)_3]^{3-}$ which shows no exchange in solution between the cobalt atoms in the complex and in the hexaaquocobalt (II) ions (Barbieri <u>et al</u>. 1957), appear to be good candidates for investigation.

At present there is only a little information on the actual mechanism of the exchange process in the solid-state. The failure of ionizing radiation to have much effect suggests that electronic processes are not very important. The positive effect of dislocations suggests that the exchange involves movement of atoms and the need is now to devise experiments that will reveal something about the nature of this movement. Of the systems so far studied the $[Co(NH_3)_5Cl]Cl_2$ seems the easiest to understand, but so far very little is known of systems of this kind and one may enquire whether all such ligand exchanges proceed by a ligand-deficient species mechanism? This question is probably the easiest to answer in the near future.

Appendix 1

The exchange law for homogeneous stable systems

Consider an exchange reaction between reactants A and B in which atoms of element X are common to both species and are exchanged at a rate R (Myers & Prestwood 1951).

Let

a be the total number of X atoms contained in reactant A in the original reaction system (active plus inactive),

b be the total number of X atoms contained in reactant B in the original reaction system (active plus inactive),

x be the number of active X atoms contained in A after a time t,

y be the number of active X atoms contained in B after a time t.

$S_A = \frac{x}{a}$ is the fraction of X atoms in A that are active at time t (specific activity).

$S_B = \frac{y}{b}$ is the fraction of X atoms in B that are active at time t (specific activity).

Let F be the fraction of exchange, defined as

$$F = \frac{S_A - S_{Ao}}{S_{A_\infty} - S_{A_o}} = \frac{S_B - S_{Bo}}{S_{B_\infty} - S_{Bo}} \qquad (1.1)$$

or

$$F = \frac{x - x_o}{x_\infty - x_o} = \frac{y - y_o}{y_\infty - y_o} \qquad (1.2)$$

where subscripts 0 and ∞ refer to $t = 0$ and $t = \infty$, respectively.

The rate of increase in the number of radioactive X atoms in reactant A is given by

$$\frac{dx}{dt} = R\,\frac{y}{b}\left(1 - \frac{x}{a}\right) - R\,\frac{x}{a}\left(1 - \frac{y}{b}\right)$$

$$= R\left(\frac{y}{b} - \frac{x}{a}\right)$$

$$= \frac{R}{ab}\,(ay - bx) \qquad (1.3)$$

$R\,\frac{y}{b}\,(1-\frac{x}{a})$ represents the rate of appearance of radioactive X atoms in A, since R is the rate of appearance of X atoms in A coming from B, $\frac{y}{b}$ is the fraction of X atoms in B that are radioactive, and $(1-\frac{x}{a})$ is the fraction of X atoms in A that are not radioactive.

$R\,\frac{x}{a}\,(1-\frac{y}{b})$ is the rate of disappearance of radioactive X atoms from A.

When exchange is complete, and neglecting isotopic effects, the fractions of active X atoms in A and in B are the same, so that at equilibrium the distribution of the tracer between the two reactants gives $x = x_\infty$ and $y = y_\infty$:

$$\frac{x_\infty}{a} = \frac{y_\infty}{b}$$

$$y_\infty = b\,\frac{x_\infty}{a} \qquad (1.4)$$

and $\quad y + x = y_\infty + x_\infty \qquad (1.5)$

If y in equation (1.3) is eliminated by substitution from equations (1.4) and (1.5), then

$$\frac{dx}{dt} = \frac{R}{ab}\,(a\,x_\infty + b\,x_\infty - ax - bx)$$

$$= \frac{R}{ab}\,(a + b)(x_\infty - x)$$

and

$$\frac{dx}{x_\infty - x} = \frac{R\,(a+b)}{ab}\,dt. \qquad (1.6)$$

The integrated form of equation (1.6) is

$$- \ln(x_\infty - x) = \frac{R\,(a+b)}{ab}\,t + \text{constant.} \qquad (1.7)$$

The constant of integration evaluated at $t = 0$ when $x = x_o$ gives

$$\text{constant} = - \ln(x_\infty - x_o). \qquad (1.8)$$

By substitution of equation (1.8) in (1.7), and rearranging:

$$Rt = - \frac{ab}{a+b} \left[\frac{(x_\infty - x_o) - (x - x_o)}{x_\infty - x_o} \right].$$

or $$Rt = - \frac{ab}{a+b} \ln\ (1 - F) \qquad (1.9)$$

where $F = \dfrac{x - x_o}{x_\infty - x_o}$, as defined in equation 1.2.

If A was initially inactive, so that $x_o = 0$, the fraction of exchange would be

$$F = \frac{x}{x_\infty}. \qquad (1.10)$$

Writing equation (1.9) as

$$- Rt\ \left(\frac{a+b}{ab} \right) = \ln(1-F)$$

and making

$$\lambda = R\ \left(\frac{a+b}{ab} \right) \qquad (1.11)$$

we have

$$\ln(1-F) = - \lambda t \qquad (1.12)$$

which is commonly known as the McKay equation, where (1-F) is the unexchanged fraction at time t.

R is the rate of exchange and depends on the order of the reaction in terms of each component of the system,

$$R = k\ a^\alpha\ b^\beta \qquad (1.13)$$

where k is the rate constant having the form:

$$k = \nu \, e^{-Ea/\kappa T} \qquad (1.14)$$

where ν is a frequency factor (s^{-1}), E_a is the energy of activation (eV), κ is Boltzmann's constant (8.6716×10^{-5} eVK^{-1}) and T is the temperature (K).

From the McKay equation (1.12), λ (and hence R) can be determined from semi-logarithmic plots of (1-F) against t which are straight lines passing through unity.

Another useful parameter is the half-time of exchange, $t_{\frac{1}{2}}$, which is the time necessary for the fraction of exchange to reach a value of one half. This can be determined from equation (1.9), substituting 0.5 for F and $t_{\frac{1}{2}}$ for t:

$$R = \frac{ab}{a+b} \cdot \frac{0.693}{t_{\frac{1}{2}}} \qquad (1.15)$$

and

$$t_{\frac{1}{2}} = \frac{0.693}{\lambda} \qquad (1.16)$$

Appendix 2

Corrections for incomplete separation of the reactants and separation-induced exchange

Prestwood and Wahl (1949) have shown that when the separation-induced exchange and the incomplete-separation effects are reproducible, the following simple relations are true:

$$F = \frac{S - S_o}{S_\infty - S_o} = \frac{F' - F_o'}{1 - F_o'}$$

where S and S_o are the specific activities of a chemical fraction enriched in one of the exchange reactants separated at time t and time zero, respectively, and S_∞ is the equilibrium specific activity of the reactant. F' and F_o' are the fractions of exchange measured after separation at times t and zero, respectively.

Their proof was as follows:

Consider an exchange reaction between the molecular species A and B in which atoms of element X, common to both species, are exchanged. Consider now that after the separation of A and B, some of the X atoms that were in species B just prior to the separation end up in species A after the separation, as a result of separation-induced exchange, incomplete separation or both.

The specific activity is defined as the ratio of radioactive X atoms to the total number of X atoms in the same molecular species or chemical fraction.

Let S_A be the specific activity of reactant A at time t and prior to the separation,

S_{Ao} be the specific activity of reactant A at time zero and prior to the separation,

S_B be the specific activity of reactant B at time t and prior to the separation,

S_{Bo} be the specific activity of reactant B at time zero and prior to the separation,

S_∞ be the equilibrium specific activity of A or B,

S be the specific activity of the chemical fraction enriched in A and separated from the reaction mixture at time t,

S_o be the specific activity of the chemical fraction enriched in A and separated from the reaction mixture at time zero,

a' be the atoms of element X that were contained in A prior to the separation and that appear in the chemical fraction enriched in A, and

b' be the atoms of element X that were contained in species B prior to the separation and that appear in the chemical fraction enriched in A.

F is the fraction of exchange at time t prior to the separation, given by

$$F = \frac{S_A - S_{Ao}}{S_\infty - S_{Ao}} \qquad \frac{S_B - S_{Bo}}{S_\infty - S_{Bo}}$$

F' is the fraction of exchange observed after separation at time t, given by

$$F = \frac{S - S_{Ao}}{S_\infty - S_{Ao}}$$

F_o' is the fraction of exchange observed after separation at time zero, given by

$$F_o' = \frac{S_o - S_{Ao}}{S_\infty - S_{Ao}} .$$

We assume that a' and b' are independent of the time of separation, i.e., that the separation-induced exchange and the degree of separation of the reactants are reproducible. Then

$$S = \frac{a'S_A + b'S_B}{a'+b'}, \qquad (2.1)$$

$$S_o = \frac{a'S_{Ao} + b'S_{Bo}}{a'+b'}, \qquad (2.2)$$

$$S_\infty - S = \frac{a'S_\infty + b'S_\infty - a'S_A - b'S_B}{a'+b'} =$$

$$= \frac{a'(S_\infty - S_A) + b'(S_\infty - S_B)}{a'+b'}. \qquad (2.3)$$

Similarly,

$$S_\infty - S_o = \frac{a'(S_\infty - S_{Ao}) + b'(S_\infty - S_{Bo})}{a'+b'} \qquad (2.4)$$

and

$$\frac{S_\infty - S}{S_\infty - S_o} = \frac{a'(S_\infty - S_A) + b'(S_\infty - S_B)}{a'(S_\infty - S_{Ao}) + b'(S_\infty - S_{Bo})}. \qquad (2.5)$$

From the definition of F

$$1 - F = \frac{S_\infty - S_A}{S_\infty - S_{Ao}} = \frac{S_\infty - S_B}{S_\infty - S_{Bo}} \qquad (2.6)$$

and $(S_\infty - S_A) = (1-F)(S_\infty - S_{Ao})$ (2.7)

$(S_\infty - S_B) = (1-F)(S_\infty - S_{Bo})$. (2.8)

Substitution of equations (2.7) and (2.8) in (2.5) gives

$$\frac{S_\infty - S}{S_\infty - S_o} = \frac{(1-F)[a'(S_\infty - S_{Ao}) + b'(S_\infty - S_{Bo})]}{a'(S_\infty - S_{Ao}) + b'(S_\infty - S_{Bo})} = 1-F. \qquad (2.9)$$

Therefore

$$F = 1 - \frac{S_\infty - S}{S_\infty - S_o} = \frac{S - S_o}{S_\infty - S_o} . \qquad (2.10)$$

Alternatively from the definitions of F' and F_o', we have

$$1 - F' = \frac{S_\infty - S}{S_\infty - S_{Ao}} \qquad (2.11)$$

$$1 - F_o' = \frac{S_\infty - S_o}{S_\infty - S_{Ao}} . \qquad (2.12)$$

and

$$\frac{1 - F'}{1 - F_o'} = \frac{S_\infty - S}{S_\infty - S_o} = 1 - F . \qquad (2.13)$$

Hence

$$F = 1 - \frac{1 - F'}{1 - F_o'} = \frac{F' - F_o'}{1 - F_o'} \qquad (2.14)$$

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