EXCHANGE BETWEEN NORMAL LATTICE OCCUPANTS

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ABSTRACT

The exchange of thallium atoms in labelled $Tl^{I}_{3}\ Tl^{III}Cl_{6}$ has been studied in the solid state. The process is hardly affected by ionising radiation but greatly accelerated by grinding. The kinetics of the exchange are complex, but compatible with three first order processes with different energies of activation. Introduction of dislocations and increase of surface by grinding does not change these energies but alters the proportions exchanging by the different processes.

Studying the thermal annealing reactions in neutron irradiated solids has appealed to some as a means of indirect elucidation of the processes following nuclear reactions in solid matrices [1]. However, in spite of a considerable wealth of data on the subject [2,3] the mechanisms of these processes are still very imperfectly understood. But since the first experiment of Kaučić and Vlatković [4] it has become clear that part of the annealing processes, at least, are of the nature of exchange processes, involving the radioactive fragment produced by the nuclear event and surrounding lattice species.

A substantial body of information has accumulated on systems in which the exchanging radioactive entity is not produced in situ by some nuclear event, but introduced, effectively as an impurity, by doping techniques, usually dependent on co-crystallisation, or by ion implantation [5]. It has been clearly demonstrated that these reactions are a variety of exchange reactions, that is to say that no over-all chemical change, beyond isotopic redistributions, accompanies the exchange reaction. An in situ proof was provided by the experiments of Nath and Klein [6] and Mahieu et al. [7] who showed that no overall chemical change accompanied the CrIII-CrVI exchange in doped chromates.

In all these experiments however one component of the exchange process was present at very low concentration, effectively as an impurity in the lattice, although randomly distributed throughout the sample - the dopant [8,9,10,11].In most cases the precise chemical identity and environment of the dopant species was a matter of conjecture. The chemical concentration of the dopant was often comparable with the concentration of some kinds of defect present in the crystal. In the ion implanted systems these difficulties were compounded by the presence of substantial concentrations of radiolytic debris.

Although there is no lack of suitable systems for study there has so far been only one report of a search for exchange between normal lattice entities. The Lazzarinis [12,13] have reported that an exchange process accompanies the dehydration of $[Co(H_2O)_6]$ $[Co\ glyc_2(NO)_2]_2 2\ H_2O$ initially labelled only in the cation. The exchange could also be initiated thermally after introduction of vacancies by gamma irradiation of the crystals.

Specifically labelled mixed valence compounds seem especially attractive for such studies. Several years ago it was established which compounds in this category could be synthesized with one kind of atom labelled and then the two kinds separated without substantial exchange being found to have occurred. Indeed the case of plumbous plumbate, the yellow oxide of lead, was one of the very early chemical applications of radioactive tracers [14]. A classification of these compounds on the basis of these and other data has been elaborated by Robin and Day [15,16]. However, there is no record of attempts to induce exchange homogeneously in such specifically labelled solid compounds.

From amongst these compounds we have selected the mixed valence thallium chloride of empirical formula Tl_4Cl_6. Although a complete crystallographic structure has not been published it seems that it contains $TlCl_6^{\equiv}$ anions and can be considered as $Tl^I{}_3(Tl^{III}Cl_6)$ [17]. It is reasonably thermally stable, being reported to melt before decomposition at 388°C [18]. Preliminary experiments confirmed that exchange between Tl^+ and Tl^{3+} in solution is slow [19,20] and that the compound could be made specifically labelled and the thallous and thallic species subsequently separated without very much exchange [21,25]. The natural ^{203}Tl yields the rather long-lived beta active and orbital electron capturing ^{204}Tl ($t_{\frac{1}{2}}$ 3.8y) upon thermal neutron irradiation, the activation cross-section being very favourable [22]. Thus experiments on both labelled and neutron irradiated material should be possible.

EXPERIMENTAL

Materials

Several methods have been described for preparing Tl_4Cl_6 [23,24]. However, these syntheses necessitate a high temperature of the reacting medium, and had to be rejected as favouring isotopic exchange. The method proposed by Mc Connell et al. [25] was also discarded, as not allowing the preparation of large enough amounts of the product. A new preparation procedure has hence been developed based on the gross reaction:

$$Tl^{III}Cl_3 + 3\ Tl^{I}ClO_4 + 3HCl \rightarrow Tl^{I}_3(Tl^{III}Cl_6) + 3HClO_4$$

$TlClO_4$ was obtained by directly attacking thallous carbonate with perchloric acid. The solution was stirred for 24 hours and the salt was purified by crystallization.

$TlCl_3$ was prepared by bubbling Cl_2 into a TlCl suspension in 6N HCl. The solution was heated near to boiling and, after the yellow intermediate dissolved, slowly evaporated under reduced pressure. The crystals were later dehydrated by $SOCl_2$ [26]:

$$TlCl_3\ 4H_2O + 4SOCl_2 \rightarrow TlCl_3 + 4SO_2 + 4HCl$$

The dehydration was conducted in sealed ampoules, at ambient temperature. The anhydrous $TlCl_3$ was stored in vacuo in sealed ampoules.

Tl_4Cl_6 was synthetized by the slow addition of $TlClO_4$ to a 0.1 M hydrochloric acid solution of 6×10^{-3} M $TlCl_3$, with continuous stirring. The 7.17×10^{-2}M concentration of the $TlClO_4$ solution was such that the final HCl concentration would not fall below 0.08 M at the end of the reaction. After a further 5 minutes stirring, the solution was cooled and deposited glittering pale yellow crystals of Tl_4Cl_6. These were washed with 0.08 M hydrochloric acid, dried and stored in vacuo. It must be noted that too rapid addition of the $TlClO_4$ solution may result in the precipitation of TlCl. Also, too high a concentration of the reactants or too high acidity of the medium may favour the precipitation of TlCl and of mixtures of Tl_2Cl_4 and Tl_4Cl_6. In the case $^{204}Tl^{I}$ or $^{204}Tl^{III}$ labelled Tl_4Cl_6, the respective labelled reactants $^{204}TlClO_4$ or $^{204}TlCl$ (further oxidated into $^{204}TlCl_3$) were both prepared from radioactive thallous sulphate solution (0.1 μCi/mg) [27]. The salts were purified by recrystallization. About 1 to 1.5% of $^{204}Tl^{III}$ was found in $^{204}TlClO_4$ after purification, using the analytical method described below, whereas no $^{204}Tl^{I}$ was detectable in the $^{204}TlCl_3$.

Induced exchange during the preparation, giving activity in the unlabelled thallium in the Tl_4Cl_6 amounted to about 5%

in most cases for $^{204}\mathrm{Tl}^{\mathrm{I}}_{3}$ ($\mathrm{Tl}^{\mathrm{III}}\mathrm{Cl}_{6}$) and to some 3% for $\mathrm{Tl}^{\mathrm{I}}_{3}$ ($^{204}\mathrm{Tl}^{\mathrm{III}}\mathrm{Cl}_{6}$).

Analytical technique and radioactivity measurements.

The $\mathrm{Tl}^{\mathrm{I}}/\mathrm{Tl}^{\mathrm{III}}$ separation has been made by the solvent extraction method proposed by Butterworth and Harbottle [20]. The sample to be analyzed was dissolved in 4cc of a 0.15 N hydrochloric solution, in the presence of 2.5×10^{-4} M Tl^{I} and $\mathrm{Tl}^{\mathrm{III}}$ chlorides as carriers. An aliquot of the the solution was removed and extracted by an equal volume of a 95 volume % methyl isobutyl ketone - n octanol mixture. After a 1.5 min. agitation, the two phases were centrifuged and equal aliquots of the two phases were taken for counting. The Tl^{I} remains in the aqueous phase, whilst $\mathrm{Tl}^{\mathrm{III}}$ is extracted by the hexone. The n-octanol serves only to facilitate the separation of the two phases. The activity was most conveniently measured using the 71 keV X-ray photopeak of $^{204}\mathrm{Hg}$, using a 2" x 2" well-type NaI(Tl) scintillator, coupled to a single channel analyser. Preliminary experiments showed 99.7% of the $\mathrm{Tl}^{\mathrm{III}}$ was extracted, and 99.6% of the Tl^{I} remained in the aqueous phase. For a given sample, the average error on determining the Tl^{I} or $\mathrm{Tl}^{\mathrm{III}}$ percentage was ± 1.2 per cent. This error grew to ± 2.8 per cent for the measured exchange on some of the samples heated for long periods. For isochronal data, however, the error in the measured exchange was less than ± 1%.

Characterization of Tl_4Cl_6.

(a) Microanalysis. Determinations of the Cl percentage have been performed at the Service Central de Microanalyse du C.N.R.S. , leading to 20.67 ± 0.2%. This percentage is consistent with the calculated value of 20.65%. Identical results have been obtained for Tl_4Cl_6 heated in vacuo from 10 hours at 209°C up to 60 hours at 270°C, thus confirming the thermal stability of the compound.

(b) X-ray diffraction. The crystal structure of Tl_4Cl_6 is unfortunately but poorly known [17]. It may be noted however, that the powder X-ray spectra of Tl_4Cl_6 were found identical before or after the thermal treatments afore mentioned.

(c) Radiometric titration. The Tl^{I}/Tl^{III} separation for the non-radioactive Tl_4Cl_6 was made by the extraction method described above. Bubbling SO_2 through the organic phase reduced the Tl^{III} to Tl^{I}, which was re-extracted by water. Carrier-free $^{204}Tl^{I}$ was added to both the Tl^{I} and Tl^{I} from Tl^{III} solutions, and the titration was conducted with a 0.1 M KI solution [28]. The equivalence point indicating the end of the reaction was detected by radioactivity measurements. For the same samples as described in (a), the results of analysis were 58.3 ± 1.7% for Tl^{I} and 18.3 ± 0.5% for Tl^{III}, agreeing with the calculated values of 59.52% and 19.81%

Sample treatments

(a) Heating. A silicone-oil bath thermostat was used with a thermal stability within ± 0.5°C, up to 300°C. The samples consisted of 3 to 6 mg. of Tl_4Cl_6, deposited in Pyrex tubes sealed in vacuo. These were immersed into the stabilized oil bath for the chosen time, then swiftly cooled in liquid nitrogen.

(b) Gamma-irradiation. The irradiations were made at room temperature, using a ^{60}Co source. The dose rate was 0.08 MRad/h, and the duration was 262h. The samples were kept in vacuum-sealed ampoules.

(c) Grinding. The samples were ground within a glove-box, under a dry nitrogen atmosphere. The N_2 stream was dried with $CaCl_2$ and P_2O_5, and the system flushed for 24 hr to avoid moisture.

Results and Discussion.

The first experiments showed that exchange took place at a convenient rate in the temperature range 180-250°C. Exchange isotherms were measured at different temperatures within this interval. It was found that different preparations of the labelled $Tl^{I}_{3}Tl^{III}Cl_{6}$, as well as showing slightly different proportions of zero time exchange, also gave rather different exchange isotherms. The differences were much greater than the errors on the measurements, so that sets of data were accumulated for a single preparation of the labelled complex. Specimen exchange isotherms are plotted on a semilogarithmic scale for the exchange percentage E (sample C), in Fig.1. Fig.2 shows the considerable difference in the exchange isotherms at 186°C for material from two different preparations (samples A and B).

Experiments were made both with samples labelled in the univalent and in the trivalent thallium. Naturally, because of the composition of the substance, greater precision in the measurements was possible with the latter technique. But both kinds of preparation showed essentially the same exchange characteristics and, taking the measured thermal stability of the compound into account, this shows that a genuine exchange reaction is involved.

A semilog plot of the data for the exchange isotherms showed that the process does not obey the usually simple $f = e^{-kt}$ rate law where f represents the fraction unexchanged at time t (Fig.1). Indeed the exchange isotherms closely resemble the annealing isotherms found for reformation of labelled parent species in neutron irradiated complexes [1] .

Now the Mackay treatment [29] shows that a genuine isotopic exchange process must follow essentially a $f=e^{-kt}$ law. However, for a solid system it permits the possibility that more than one value of k is involved. Thus different situations in the crystallites may have different energies of activation, E_a, and, or, different frequency factors, ν , for the exchange process, for which $k = \nu e^{-E_a/T}$. One can envisage both a simple line spectrum or a continuous spectrum of E_a and, or, ν .

In the simplest case, for instance, one could have a fraction p of the thallium exchanging with activation, energy E_a and the remainder with an energy E_a' . Kinetic patterns of this kind seem to be very characteristic of processes occuring in solids in a quasi-homogeneous fashion [30].

To facilitate the identification [30] of the spectrum of kinetic parameters an exchange isochronal was measured over the whole temperature range. The constant time of heating of the samples was 21 minutes. The result is shown in Fig. 3 (sample C). The slope of this isochronal clearly shows that more than one energy of activation must be involved.

Since several of the doped exchange systems have been shown to be sensitive to the nature of the ambient atmosphere during the exchange process [31], a comparison of samples heated in air and in vacuo was made. The values obtained, indicated on Fig. 3 , show that this system is not appreciably affected by the ambient atmosphere. Very likely sensitivity to the ambient atmosphere will prove to be a characteristic only of the system where one exchanging reactant, the dopant, is present at very low chemical concentration.

The kinetic characteristics of most annealing reactions following neutron capture in a crystalline solid, as well as the exchange in the doped system, are influenced by the defects present in the material [32]. Thus an ionising irradiation of the system as well as producing some exchange sensitises the system to further thermal exchange. The sole case of exchange between normal lattice entities explored by the Lazzarinis [12,13] was also profoundly affected by an ionising irradiation with ^{60}Co gamma radiation. The neutron irradiated systems are also usually affected by the kind of defects introduced by grinding the crystals. A comparison was therefore made of untreated labelled $Tl^{I}Tl^{III}Cl_6$, material irradiated with ^{60}CO radiation to a dose of 21 M rad and finally a sample from the same preparation that was ground before use. All three samples were heated at 209°C. Figure 4 shows the results. It is apparent that the ionising irradiation has no very marked effect on the progress of the exchange. (Fig. 4).

This experiment leads to several interesting conclusions. Firstly, from a formal point of view the $Tl^{I} - Tl^{III}$ exchange could occur in the $Tl^{I}_{3} Tl^{III} Cl_{6}$ by a purely electronic process. If such a process were indeed possible it should be initiated by ionising irradiation. It is concluded that although exchange without movement of thallium atoms is a priori a possibility, it does not occur. Indeed such a mechanism would probably involve too great a disturbance of the electrostatic energy of the crystal. Thus this observation suggests that the exchange must involve physical interchange of Tl atoms.

The overlap of the exchange isotherms for the normal and gamma irradiated material shows that not only does the irradiation fail to bring about exchange but it does not facilitate subsequent thermal exchange. In this respect our system is very different from most doped or neutron irradiation generated systems. Most probably the difference can be attributed to the fact that in these other systems one of the exchanging entities is present at a concentration not greatly different from that of the defects generated by the ionising irradiation. Both ambient atmosphere and point defect sensitivity may well be characteristic of exchange with one reactant at a very low concentration, the defects behaving effectively as reactants at one stage of the exchange process.

The effect of grinding, however, is very marked. Since the ionising irradiation, which probably introduces various point defects into the crystals, had little effect, it seems more reasonable to attribute the effect of the grinding to the enhanced dislocation density and, perhaps, greater surface area of the ground material.

Quantitative examination of the data. It is not possible to treat such data if both E_a and ν can assume more than one value. It will be assumed therefore that ν can be taken as constant. One would expect that ν would assume a value of about 10^{13} corresponding to a lattice vibration frequency. An analysis of the isochronal data on sample C taking $\nu = 7.5\ 10^{12}$ gave a significantly better fit with three energies of activation than with two, but was not markedly improved by increasing to four energies.
The values were

E_a^1 = 1.52 eV, 9.3%; E_a^2 = 1.64 eV, 26.7% and
E_a^3 = 1.71 eV, 64.0%

It may be remarked that the resolution of a Vand-Primak analysis is ca ± 2 kT, which is only a little less than 0.1 eV in this temperature region, so that bearing in mind the precision of the data one can barely distinguish the close three line spectrum of energies of activation indicated above from some continuous distribution over the same energy interval. However, using Occam's razor, we prefer the simpler line spectrum solution. Indeed computer simulation of various continuous distributions gave no better fit to the experimental data than the three discreet energies of activation.

A number of other samples gave substantially the same proportions exchanging by the different routes. These data included a sample in which the exchange was followed by labelling the Tl^{I} [33].

Perhaps the most interesting of the quantitative results obtained in this study concerns the kinetic parameters extracted for the ground material compared with those for the untreated preparation. An untreated sample that gave data fitting $E_a^1 = 1.50$, 18.2% and $E_a^2 = 1.72$ eV 81.8% after grinding gave the kinetic parameters $E_a^1 = 1.51$ 52.8% and $E_a^2 = 1.72$ eV 47.2%. A similar change, that is to say an increase in the proportion exchanging by the low activation energy process, but little or no change in the activation energies themselves, was found on grinding the sample C, referred to above.

It seems most likely that the low energy exchange mechanism involves the use of dislocation, or surfaces, of the crystallites.

For the sample C there was not only the isochronal data but also a considerable body of isothermal exchange data. In these circumstances it is possible to use an iterative programme to establish the E_a, their proportions and the frequency factor ν. When this was done a much larger value of ν and larger values of the E_a were obtained. For instance, for sample C, $\nu = 1.23 \cdot 10^{18}$ with $E_a^1 = 2.00$, 11.1%; $E_a^2 = 2.16$, 31.3% and $E_a^3 = 2.27$, 57.6%; Although the values change, the same conclusions can be reached as drawn above. The proportions found are substantially constant, the spacing, in eV, is hardly changed and grinding still increases the proportion exchanging by the lowest energy route.

Such high frequency factors are a disturbing, but by no means new, feature [34,35]. They arise largely because of the data for long exchange times on the isothermals. It should be noted that these points are liable to an appreciable larger error than the earlier points on the isothermals. Further the improvement in fit on choosing the combination of a high frequency factor and higher E_a values is much more noticable for the isothermal than for the isochronal data. The uncertainty in the calculated ν is substantial, rather worse than an order of magnitude. Nonetheless it does appear that these data, as well as other data on annealing processes in solids, are better fitted with a remarkably high frequency factor.

It appears that the exchange data require three or more energies of activation for adequate characterisation. The proportions of the exchange proceeding by the different paths varies from preparation to preparation and, on grinding a sample, the fraction able to exchange by the lower energy of activation path is markedly increased. The exchange involves some movement of thallium atoms.

This quasi-homogeneous exchange process occurring in a crystal matrix between normal lattice species seems to represent a new kind of kinetic study which shows many of the peculiarities of the post-irradiation transformation in neutron irradiated solid compounds.

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Figure captions

Fig.1. Exchange isotherms of $Tl^{I}_{3}[^{204}Tl^{III}Cl_{6}]$ (sample C). □, 180°C; ▲, 190°C; ○, 200°C; ■, 209°C; Δ, 216°C; ●, 250°C.

Fig.2. Exchange isotherms of $Tl^{I}_{3}[^{204}Tl^{III}Cl_{6}]$. Temperature: 186°C. ○, sample A; ●, sample B.

Fig.3. Exchange isochronal of $Tl^{I}_{3}[^{204}Tl^{III}Cl_{6}]$ (sample C). Time: 21 min. ○, in vacuo; ●, in air.

Fig.4. Exchange isotherms of $Tl^{I}_{3}[^{204}Tl^{III}Cl_{6}]$. Temperature: 209°C. ○, untreated; ●, gamma-irradiated (21 MRad); □, ground.

Fig. 1 -

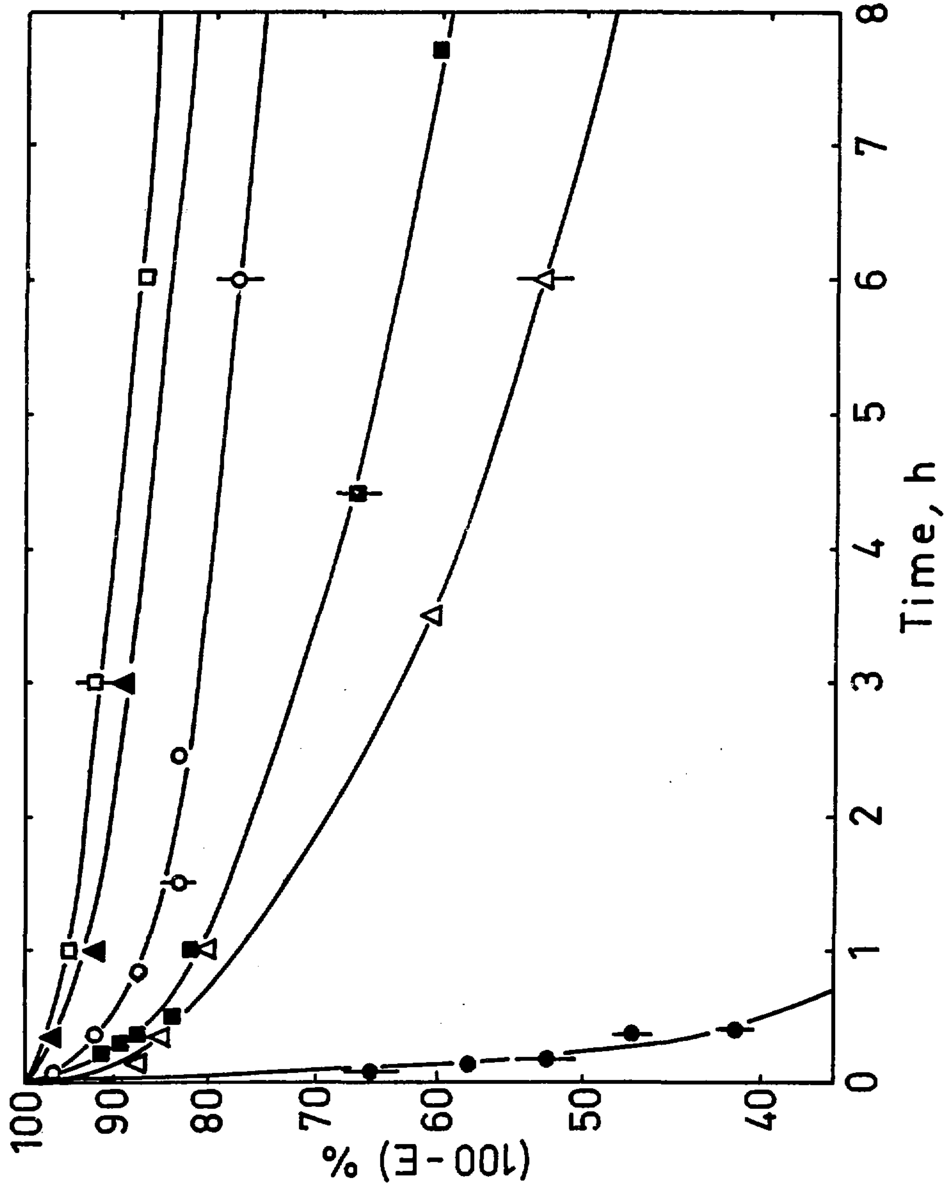

Fig. 2 -

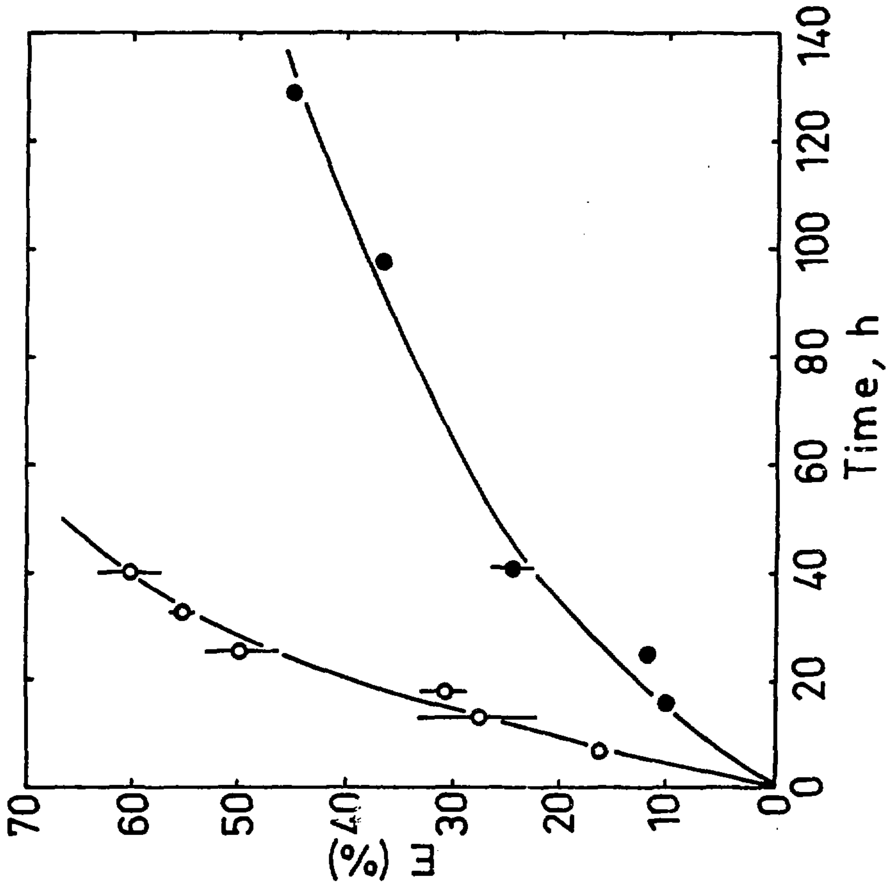

Fig. 3 -

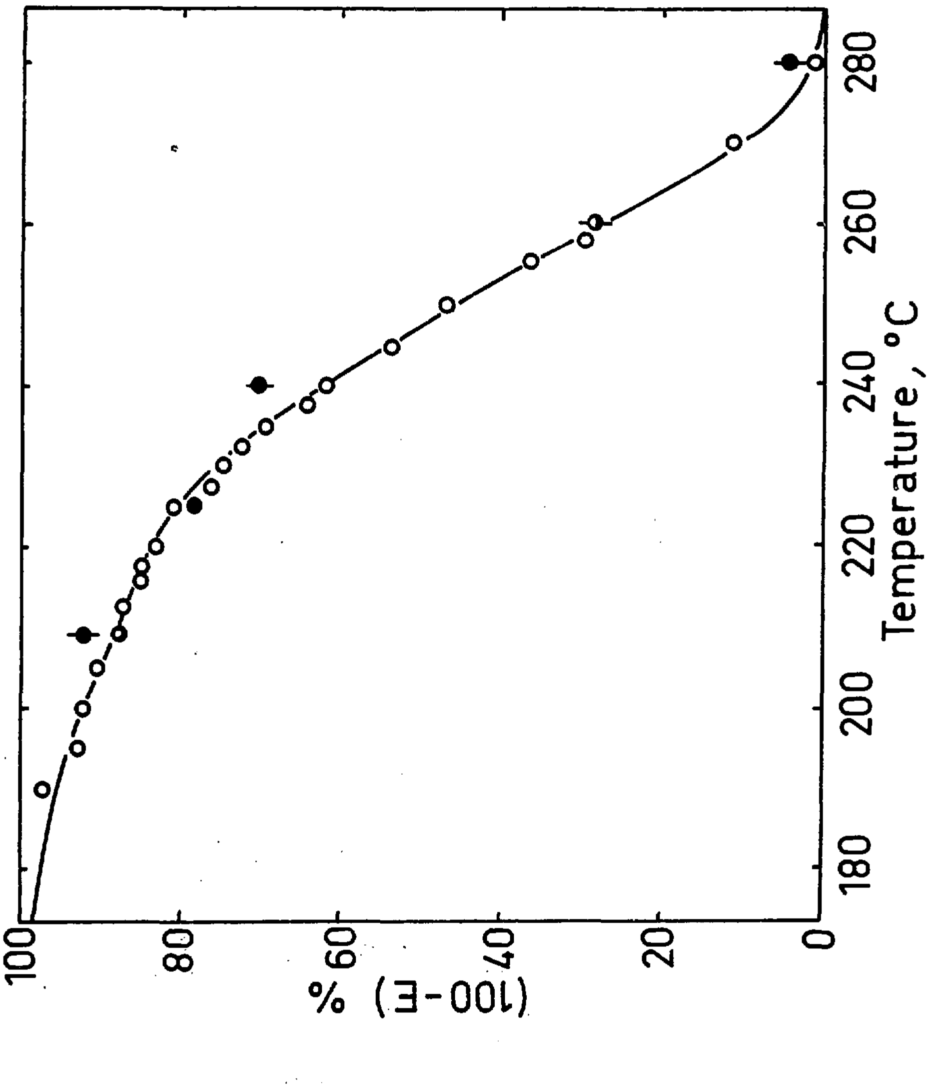

Fig.4