SOME ASPECTS OF THE ION EXCHANGE CHEMISTRY OF IODINE AND ITS COMPOUNDS

by

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ABSTRACT

The object of the work was to investigate the sorption of iodine from aqueous solutions on to a number of selected ion exchange resins.

Investigations had shown that molecular iodine was the most important species found to exist in aqueous and acidic solutions in nuclear technology, although some ionic iodine species, such as iodide and iodate, could also exist under certain circumstances.

The uptake of molecular iodine on to ion exchange resins and hydrocarbon beads was studied. The iodine adsorbed to some extent on to all of these by a charge transfer mechanism. This reaction was found to be particularly strong in aqueous solution with a polyvinyl pyridine based resin. The distribution and kinetics of iodine sorption was therefore examined in detail. Adsorption was slow and depended on crosslinking and nitric acid concentration. An empirical rate equation was derived which allowed the extent of iodine adsorption with time to be predicted.

An investigation of the adsorption of iodide from aqueous solution and iodate from aqueous and nitric acid solutions was carried out.

Iodide did not adsorb on the freely basic form of the polyvinyl pyridine resin, but some adsorption did occur on the nitrate form of the resin, possibly as a result of oxidation of the species within the pores of the resin phase.

Iodate exchange increased with increasing nitric acid concentration and resin crosslinking.

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INTRODUCTION

SECTION ONE.

1. INTRODUCTION

1.1. IMPORTANCE OF IODINE IN NUCLEAR TECHNOLOGY

Fission product iodine has long been one of the major problems in nuclear technology. It occurs throughout the industry (Fig. 1.1) with all its associated difficulties.

The reason for its importance is threefold:-

1.1.1. Its chemical properties,

1.1.2. As a health hazard,

1.1.3. Its high fission yield.

Each category will be discussed in some detail.

1.1.1. Iodine Chemistry (1,2,3)

Iodine is a dark grey solid with a metallic lustre. At atmospheric pressure it sublimes to give a violet vapour. It is slightly soluble in water but readily soluble in many organic solvents. The colour of the solution depends upon the solvent; violet in non-polar solvents such as carbon tetrachloride, brown in unsaturated hydrocarbons, and oxygen and nitrogen containing solvents such as benzene, ethanol and pyridine.

Naturally occurring iodine is monoisotopic consisting of the nuclide Iodine-127. Some other properties are summarised in table 1.1.

Although the chemistry of iodine is essentially non-metallic, i.e. the formation of I^- or a single covalent bond -I, there is good evidence of cationic species (eg. I^+ in liquid BrF_3 and SO_2; I^{3+} in acetic anhydride as $I(CH_3CO_2)_3$). Higher covalencies with formal oxidation states up to +7 are known, eg. periodate, IO_4^-.

A particularly important point in all iodine solution studies is the phenomenon of charge transfer. With many donor solvents, iodine forms a

1:1 complex of the form I_2---S. The bonding energy is attributable to a partial sharing of charge.

1.1.2. Iodine as a Health Hazard

In considering radioiodine as a health hazard, several factors are of importance:-

(i) The only nuclides of greater than one day half life which are formed in the nuclear reactor are I^{127}, I^{129} and I^{131}. I^{127} is stable and causes no hazard. I^{129} has a half life of 1.7×10^7 years (4), and this is very long compared to the biological half life of 90 days. Hence I^{129} will cause little hazard. I^{131} has a half life of 8.0 days (4) and this is the only nuclide to constitute a biological hazard in any accidental release.

(ii) A second factor is the physical origin and dispersal of released iodine. Holland (6) and Perkins (7) consider the general sources of radioiodine arising in nuclear reactors, fallout and reprocessing facilities. The volatility of iodine aids in its dispersion (8), although it is adsorbed onto surfaces, dust and fumes, and reacts with trace constituents in the atmosphere (9). Iodine remaining in a dispersable form in the vapour phase can exist in several physical and chemical forms (7), e.g. as elemental iodine, as hydrogen iodide, as an iodate or other iodide.

(iii) The mode of uptake of iodine is also important. The ingestion of contaminated foods, in particular milk, is responsible for the accumulation of iodine in the body. (5, 10, 11). Iodine is selectively concentrated in the human thyroid. The fraction passing from the gut to the thyroid is thought to be circa 0.3% (5).

(iv) A further factor to consider is the effect on the body of concentrating I^{131} in the thyroid. The accumulation of radioiodine in the body can lead to partial or total destruction of the thyroid gland, or to

carcinoma (12). Normal thyroid activity is essential to the well-being of the individual.

(v) Methods of eliminating iodine or preventing uptake and retention are clearly important. Compounds such as iodide, chlorate, thiouracil and carbimazole can be used to block iodine uptake by the thyroid (13) in situations where it is not feasible to prevent radioiodine being ingested. Graul et al (14) found that the most effective treatment was gastric lavage (with injection of $KClO_4$) for the first few hours after I^{131} ingestion. After 24 hours, optimal results were obtained using thyroid stimulating hormones combined with potassium chlorate.

Apart from these important considerations concerning radioiodine, the dangers from inactive iodine should not be minimised as death or permanent injury can result from very short exposures (15, 16).

1.1.3. Fission Yields of Iodine

The slow neutron fission yield of iodine-131 from Uranium is approximately 3% (17).

Comparison of the fast fission yield for iodine isotopes from plutonium-239 is shown in Table 1.2 (18).

It can be seen that iodine occurs in a considerable yield. Usually, a cooling period of greater than 100 days has been used to ensure virtually complete decay of I^{131}. With a plutonium fuel such a long cooling period may not be economically desirable and iodine will become a major problem in the reprocessing cycle.

In summary, it can be seen that iodine is a reactive element, a serious health hazard and occurs in a high fission yield.

1.2. THE ROLE OF IODINE IN NUCLEAR TECHNOLOGY

In the previous section the reason for the importance of iodine has been shown. In this section the exact nature of the iodine problem will be traced throughout the reactor and fuel reprocessing cycles.

1.2.1. Reactor Systems

A nuclear reactor consists basically of a matrix of fissile material. The heat of fission is utilised to generate a working fluid (usually steam), which operates a turbine in order to produce electricity. Many such reactor systems have been developed for power production and for research.

1.2.2. Occurrence of Iodine Within Reactor Circuits

For the purpose of this discussion the main feature of interest is the fate of any accidental iodine release. The form of iodine produced in the fuel during irradiation will depend on the nature of the fuel. With uranium metal fuels, Rupp et al (22) suggested that iodine occurred as atoms of zero valency or as molecular iodine. In an inert atmosphere Castleman et al (19) considered iodine to occur as uranium iodides (UI_z). In air, elemental iodine will be released:-

$$3UI_z + 4O_2 \longrightarrow U_3O_8 + 3zI$$

In dry air uranium iodides may be oxidised to uranyl iodide (UO_2I_2) and iodine. Bagnall (20) in a discussion on actinide halides thought that this mechanism was doubtful. It would seem therefore that molecular iodine is the most important species to be formed within a metal fuel.

Similarly, molecular iodine is likely to be the main species formed within an oxide fuel. The environment will be more oxidising in nature but it is unlikely to be sufficiently so as to cause the formation of iodates.

Even under normal conditions there are trace amounts of activated corrosion products and fission products present in the coolant, and a rapid build up of fission products could occur as a result of a fuel can failure. This could lead to more corrosion of the coolant circuit and interfere with any coolant purification system. Iodine, being extremely reactive, volatile and corrosive, would be a particularly serious problem. It is important therefore to study the likely form of iodine in such a circuit and also methods of removing it.

1.2.2.a. Liquid Cooled Reactors

The concentration of iodine in the circuit would be extremely small, the actual value depending on the nature of the contamination, but never greater than 10^{-5} mol. dm^{-3}. Castleman et al (39) discussed possible species and concluded that the final form depended on the environment. In neutral or oxidising conditions I^{o} (largely elemental) appeared to be present, whereas in reducing conditions I^{-} existed. They, however, thought that it was likely that certain unspecified forms were also present.

Eiland and Kahn (40) found that the oxidation of iodine in concentrations of circa 10^{-7} mol.$dm.^{-3}$ produced several uncharacterised species, and suggested that these were in the +2 or +3 oxidation states.

Kahn and Wahl (41) investigated chemical forms of iodide (initially) at low concentrations (10^{-7} mol.$dm.^{-3}$) using I^{131}. They oxidised these solutions under different conditions. This resulted in the formation of I_2 and three unidentifiable species, none of which were exchangeable with I^{-}, I_2 or IO_3^{-}. They suggested that reactions with trace impurities may have been responsible for some of these species.

Good et al (42, 43, 44) investigated possible species in depth. They did this using tracer and spectrophotometric techniques on an organic-aqueous system (CCl_4 - H_2O, CS_2 - H_2O) with elemental iodine. At lower

concentrations, i.e. below 10^{-3} mol. $dm.^{-3}$, the distribution coefficient fell rapidly. This was explained by considering the following reactions:-

(i) Iodine forms a brown solution in water, indicating a charge transfer complex:-

$$I_2 + H_2O \rightleftharpoons H_2O.I_2 \quad (1)$$

(ii) In dilute solutions this equilibrium lies to the right and the complex formed will dissociate:-

$$H_2O.I_2 \rightleftharpoons H_2O.I^+ + I^- \quad (2)$$

(iii) Further reactions will occur:-

$$I^- + I_2 \rightleftharpoons I_3^- \quad (3)$$

$$H_2O.I^+ \rightleftharpoons HOI + H^+ \quad (4)$$

Overall, new species formed will be HOI and I_3^-. Normally hypoiodous acid disproportionates to iodide and iodate:-

$$3HOI \rightleftharpoons IO_3^- + 2I^- + 3H^+ \quad (5)$$

but it is increasingly stable at low concentrations and no iodate could be detected.

Katzin (45) suggested that in a similar system to the one used by Good et al, a species involving a transfer of charge between iodine atoms might be formed, i.e. of the $H_2O.I^+I^-$ type.

Chia (46) doubted that $H_2O.I^+$ could exist in preference to H_3O^+ in aqueous solutions.

The above conclusions can be applied to the coolant circuit of a water reactor. It would seem likely therefore that iodine released into such a

system would be in the molecular form (I_2). In solution this would remain mainly in this form but some I_3^- and HOI could be formed by the mechanism postulated by Good et al.

The removal of iodine from aqueous solutions in the event of coolant contamination could prove to be difficult. Most iodine removal processes are based on the ease with which it can be fixed onto a wide range of adsorbents (86, 96-103). This adsorption is slow and not completely reversible. For instance Kipling and Parkinson (99) investigated the adsorption of iodine by carbon blacks. The process took 24 days to complete.

Harley et al (97) found that iodine was adsorbed from aqueous solution onto polythene, and 20% of the iodine could not be removed.

Kipling et al (100) and Talboy (96) suggested that iodine was adsorbed by a process of chemisorption onto carbon blacks and metal surfaces.

Any iodine present in reactor coolants must be removed quickly otherwise it will interfere with the accessibility and safe maintenance of the system due to adsorption onto structural and other components. Ion exchange materials are widely used for the purification of coolant (164). It is not desirable that iodine should be allowed to build up irreversibly on the resin since this may lead to the formation of iodides (104, 105) and consequent radiation and chemical damage. Reversibly held iodine will lead to further contamination of the reactor coolant circuit. It is therefore desirable to remove iodine before it comes into contact with the main resin bed. Adsorbents such as metals, carbon etc. do not seem to be completely satisfactory for this purpose because of their low capacity for iodine.

1.2.2.b. Gas Cooled Reactors

The most likely gaseous iodine species to be released into the coolant are I_2, HI and CH_3I with the former predominant (95). Berry (95) found that the following materials were the most promising scavengers:-

(i) Vinylpyridine - butadiene co-polymers.

(ii) Epoxy polyamides.

(iii) Polyaminoacrylates.

(iv) Aromatic amines.

(v) Amine coatings using metallic reactive fillers.

(vi) High surface area coatings.

Various metals (e.g. silver, silver-copper ribbon), activated charcoals and molecular sieves have also been suggested for use in the removal of iodine vapour (9, 87-92). Decontamination factors ranged from 2,000 (88) to 20 (91).

Iwai et al (93) reported that a decontamination factor of 3.5×10^3 was obtained with "Amberlite IRA - 400 - OH", a typical strong base ion exchange resin in the hydroxide form.

Davies (94) described mechanisms of iodine sorption and suggested that dissociation occurred at metal and metal oxide surfaces resulting in chemisorption.

It appears from this work that the best materials for removing volatile iodine from the vapour phase are polymeric ~~hydrocarbons~~ materials, such as "Amberlite IRA - 400 - OH" and polyvinyl pyridine. Nitrogen containing polymers appear particularly suitable.

1.2.3. Cooling Ponds.

Spent nuclear fuel elements are unloaded into pits or canals, where they are quenched with cooling water and stored to allow some fission product activity to decay before being returned for reprocessing. The water in these ponds is usually demineralised to remove any radioactive materials (164). The discussion on liquid coolant problems in reactors will therefore also apply to this phase of the process.

1.2.4. Nuclear Fuel Reprocessing

Many methods have been used for the reprocessing of nuclear fuels (29, 38, 47-51). Basically the spent fuel is dissolved and the resulting solution is subjected to a wet chemical process in order to decontaminate the fissile material from fission products. The primary separation process is usually carried out by solvent extraction although ion exchange has been suggested as an alternative. It is possible that a combination of solvent extraction and ion exchange could be used in reprocessing fuels with a high plutonium content (165). The occurrence of iodine throughout the reprocessing cycle will be discussed below.

1.2.4. (a) Dissolving Stage

The abundance of the various iodine isotopes will depend on the extent of cooling and on the type of fuel used (section 1.1.3). The dissolving conditions will determine the iodine species formed.

Brown (21) made the following points:-

(i) The iodine present in the dissolver was mainly elemental. Initially some iodate and higher oxidation states might be present.

(ii) A decontamination factor of up to 100 could be obtained in the dissolver by removing the elemental iodine.

(iii) Elemental iodine still remains a major problem, however, since

it appeared that disproportionation reactions occurred leading to the reformation of elemental iodine.

(iv) After this decontamination, the iodine solution concentration was of the order of 10^{-6} mol. $dm.^{-3}$ and several uncharacterised species seemed to be present.

Rupp (22) discussed the behaviour of iodine during the dissolving of a uranium fuel. 30% of the iodine was given off during this stage, and air and steam sparging removed a further 50%. The remaining 20% was evolved very slowly.

Dreher et al (23) said that the evolution of iodine from uranyl nitrate solution was principally influenced by the concentration of iodine and was independent of the concentration of nitric acid or uranyl nitrate. This mechanism was approximately second order, with respect to the concentration of iodine. Added iodide or iodate was quickly liberated without exchange from the dissolver. Hence, it was concluded that the fission product iodine existed as a complex ion with an oxidation state higher than elemental.

Glendenin (24) agreed with the finding that exchange between freshly formed radioiodine atoms and carrier was slow and incomplete.

Freed et al (25) discovered that by careful control of the oxidation-reduction potential during oxidation of U^{4+} to UO_2^{++}, iodine could be distilled out of the dissolver at a rate proportional to the iodine concentration until this fell to circa 500 $\mu g.dm.^{-3}$ (4×10^{-6} $mol.dm.^{-3}$) when the rate decreased rapidly.

Rupp et al (22) suggested that iodine probably occurred within uranium metal and on dissolving, the immediate surroundings could be oxidising, i.e. nitrous acid solution, or reducing, i.e. the surface of the uranium metal. Any reduction to iodide would tend to be of short duration during

the first stages of dissolving. Some of the couples are listed below:- (26)

$$U + 2H_2 = UO_2^{++} + 4H + 6e. \quad E^o = 0.82v \qquad (6)$$

$$2I^- = I_2 + 2e. \quad = -0.53v \qquad (7)$$

$$I^- + H_2O = HIO + H^+ + 2e^-. \quad = -0.99v \qquad (8)$$

$$I^- + 3H_2O = IO_3^- + 6H^+ + 6e^-. \quad = -1.09v \qquad (9)$$

$$NO + H_2O = HNO_2 + H^+ + e^-. \quad = -0.99v \qquad (10)$$

$$NO + 2H_2O = NO_3 + 4H^+ + 3e^-. \quad = -0.96v \qquad (11)$$

Equilibria could be set up which varied throughout the dissolving stage.

$$I^- \rightleftharpoons I^o \rightleftharpoons IO^- \rightleftharpoons IO_3^- \qquad (12)$$

$$IO^- \rightarrow I^-$$

As elemental atoms were formed, two atoms would be united to form volatile molecular iodine, which was then removed from the system. Conditions early in the dissolving stage (boiling 70% nitric acid) were conducive to the oxidation of iodine to iodate (23, 27).

The energy available for the oxidation of iodine to iodate was corrected for concentrations other than 1 mol. $dm.^{-3}$ as follows:-

$$E = E^o - \frac{0.059}{3} \log \frac{(NO_3)\,(H^+)^4}{(NO)\,(H_2O)^2} \qquad (13)$$

There was sufficient energy for nitric acid to oxidise iodide directly to iodate; however, the intermediate reaction indicated in equ. (8) was probably favoured. The hypoiodite that was formed then decomposed:-

$$3HIO = 2HI + HIO_3 \quad (14)$$

Iodate and iodide react to form elemental iodine in acid solution.

Nitrous oxide during the latter dissolving stages oxidises iodide to elemental iodine, and would also tend to reduce iodate to elemental iodine.

It was thought possible that the iodate formed early in the dissolving cycle survived the balance of operations on the dissolver solution. However, it was not possible to positively identify iodate in the 10 - 20% iodine which remained in the dissolver after sparging.

Stoeller and Richards (28) indicated that 50 - 80% of iodine was evolved as 'off gas', and suggested that the best way to avoid difficulties was to use a long cooling period.

Rairey et al (29) required to process fuel after less than 90 days cooling and found that 30 - 60% of I^{131} was volatilised in the dissolver. This led to solvent build up of I^{131}. Addition of potassium iodide and sodium thiosulphite converted the iodine to a non-extractable form. The overall decontamination factor was at least 10^7. However, scale-up to pilot-plant size showed that non-characterised iodine species were formed. Mercury could not be used as a dissolver catalyst because of the high extractability of complex mercury iodides. The addition of KI followed by boil-down of the aqueous wastes resulted in the puncture of stainless steel piping in the 'off gas' system by wet iodine crystals.

Maek and Rein (30) stated that "fission product iodine exists in a multitude of oxidation states".

Lefort (31) found that irradiation of iodide solution with α particles led to the production of molecular iodine. No iodate could be detected.

Zaitseva and Chung (32) dissolved irradiated accelerator targets and found periodate, iodate and elemental iodine.

Three points were cited in Report No. KR-126:-

(a) Removal of iodine by sparging at high temperatures was to be preferred, since I_2, I^- and IO_3^- might all have been present. The sparge composition had little effect on iodine removal (33).

(b) Iodine was readily extracted into the organic phase, and therefore the cooling period for fuel should be greater than 100 days (34).

(c) Isotopic exchange has been utilised in fast reactor reprocessing to delay the solvent pick-up of I^{131}. Iodine was found to be present in all streams (35).

Holm (36, 37) considered iodine was more likely to be present in uranium metal fuel solutions as iodide, iodine or iodate (overall iodine concentration approx. 10^{-5} mol. dm^{-3}.) Tests were carried out to remove the iodine from uranium solutions by air sparging, percentage removals were as follows:- iodide 65%, elemental iodine 73%, iodate 65%. Temperature, the nature of the spargent, uranium, nitric acid and uranyl nitrate concentrations were all found to effect the removal of iodine.

Blake (38) reported that workers at Dounreay found that 95% of the iodine in their 88 day cooled uranium-molybdenum alloy fuel was volatilised during the dissolving step. About half of the remaining iodine was extracted by the solvent and was retained after scrubbing, stripping and washing. This iodine was largely elemental. Blake also stated that iodide was oxidised to elemental iodine in 2 to 3 mol. $dm.^{-3}$ of nitric acid. Sparging with air reduced the nitrous acid content, and the rate of oxidation was decreased. When the aqueous phase was shaken with an extractant (e.g. 1 mol. $dm.^{-3}$ TBP in n-dodecane), the oxidation took place very rapidly and all of the iodine was extracted. Addition of a holding reductant, sodium thiosulphate, prevented

oxidation of the I^- to I_2 in 3 mol. $dm.^{-3}$ of HNO_3. Neither ~~No~~ iodate nor periodate was found in 2 - 3 mol. $dm.^{-3}$ of HNO_3 solution. Traces were found in 12 mol. $dm.^{-3}$ of HNO_3 that had been in contact with iodine crystals for 16 hours. Possibly IO_3^- and/or IO_4^- were present in dissolver solutions.

From these discussions, it seems likely that the bulk of the iodine present in the dissolving step will be elemental. This will be partially removed, leaving a solution containing uncharacterised species as well as elemental iodine. Small proportions of iodate and periodate may also be present.

The nature of these species has not been determined. The discussion of species in water reactors (section 1.2.2.a) does, however, offer some clues as to their nature. It is possible that in acid solution the mechanism suggested by Good (equations (1) to (4)) may occur. Restating equation (2):-

$$H_2O.I_2 \rightleftharpoons H_2O.I^+ + I^- \qquad (2)$$

This dissociation would be favoured because I^- would be continually removed by re-oxidation to molecular iodine. Also in equation (4):-

$$H_2O.I^+ \rightleftharpoons HOI + H^+ \qquad (4)$$

this dissociation would not be favoured because of the high acid content. Hence under dissolving conditions the species $H_2O.I^+$ might be stabilised.

1.2.4.(b) Solvent Extraction Stage

The chemistry of iodine (section 1.1.1) is such that iodine is readily extracted into organic solvents. For a short cooled fuel of high activity the radiation dose to the solvent due to iodine can be high.

Blake (38) and Davies (52) considered shorter cooling periods could be used, provided solvent aqueous residence times were kept low.

Salmon and Lopez-Menchero (53) pointed out that the problem was unresolved for higher burn-ups of fuel and hence higher dose rates to the solvent.

Jones (54) considered that the main problems with a 30 day cooled fast reactor oxide fuel would be precipitate formation, low decontamination factor for iodine and plutonium oxidation.

Keen and Alcock (55) discussed the reaction of fission product iodine with solvents. They concluded that iodine reacted with all the solvents that they had studied and that there was little hope of removing bound iodine. They suggested that further work should be directed towards the removal of iodine in the dissolver or by preliminary extraction.

Smith (56) and Cederberg and MacOueen (57) found that mercuric salts added to the dissolver helped to suppress iodine release by a factor of ten. Unfortunately, the complex iodides formed were readily extracted into solvents (29).

These contradictory data shows that the problem of iodine removal from short cooled fuels has not yet been solved.

1.2.4.(c) Ion Exchange Stage

Little work has considered the effect of iodine on the use of ion exchange in relation to fuel reprocessing.

The ion exchange of iodide has been thoroughly studied in connection with nuclear fall-out (58-62) and also for analytical purposes (63, 64).

Kraus and Nelson (65) gave a general discussion on anion exchange and mentioned that iodide uptake decreased with increasing acid concentration and that elemental iodine was "strongly adsorbed".

Other work on elemental iodine has shown that the iodide form of a strong base resin will remove it from solution as a polyiodide (66-71).

Bhat and Rao (71) found that iodine went onto resins either by adsorption

or by the formation of iodides.

Generally, it would seem that iodine would be a problem in any ion exchange separation of nuclear fuel solutions. However, since it is often only removed in small concentrations (resin capacity 0.1 mmol.g^{-1} in reference 71), it might not prove to be such a serious problem in itself, when considering ion exchange as a means of separation for short-cooled fuels.

1.3. SUMMARY OF THE ROLE OF IODINE IN NUCLEAR TECHNOLOGY

(i) Iodine will be formed within a nuclear fuel as atoms of zero valency which will mainly combine to form molecular iodine.

(ii) It can be released into reactor coolants as molecular iodine or iodides (methyl and hydrogen iodide in gas reactors). Uncharacterised species may also be present.

(iii) The removal of iodine from liquid and gaseous coolants could prove difficult.

(iv) Iodine may be released into cooling pond water. Its presence will interfere with any demineralisation process.

(v) On dissolving fuel elements, gaseous iodine will be given off and iodine species (mainly molecular) will remain in the dissolver solution.

(vi) Reprocessing by solvent extraction will lead to a build-up of iodine in the solvent stream. If a short-cooled fuel is to be reprocessed iodine will cause considerable solvent degradation.

(vii) Iodine will be adsorbed by any ion exchange material. The amount adsorbed will probably be less than the amount taken up by a solvent.

(viii) Iodine will occur in all process streams. For a long-cooled fuel this will not be a serious problem. For a short-cooled fuel iodine-131 will become an increasingly important factor.

The preceding discussion has indicated some of the major problems associated with iodine in nuclear technology.

The purpose of this work was, in the first instance, to investigate the behaviour of iodine species in an ion exchange process. Ion exchange cycles may prove to be useful as a first stage in the reprocessing of high plutonium content fast reactor fuels (139).

The work also has a wider application in the removal of iodine species from aqueous solutions in general.

TABLE 1.1

SOME PHYSICAL PROPERTIES OF IODINE

Bond Energy	148.6 kJ mol^{-1}
First Ionisation Energy	16.7 x 10^{-19} J
Electron Affinity	5.3 x 10^{-19} J
Electronegativity	2.21 (Allred-Rochow)
Covalent Radius	0.133 nm
Ionic Radius	0.216 nm
Melting Point	386^{o} K
Boiling Point	456^{o} K
Electronic Structure	(Kr) $4d^{10}$ $5s^{2}$ $5p^{2}$

TABLE 1.2

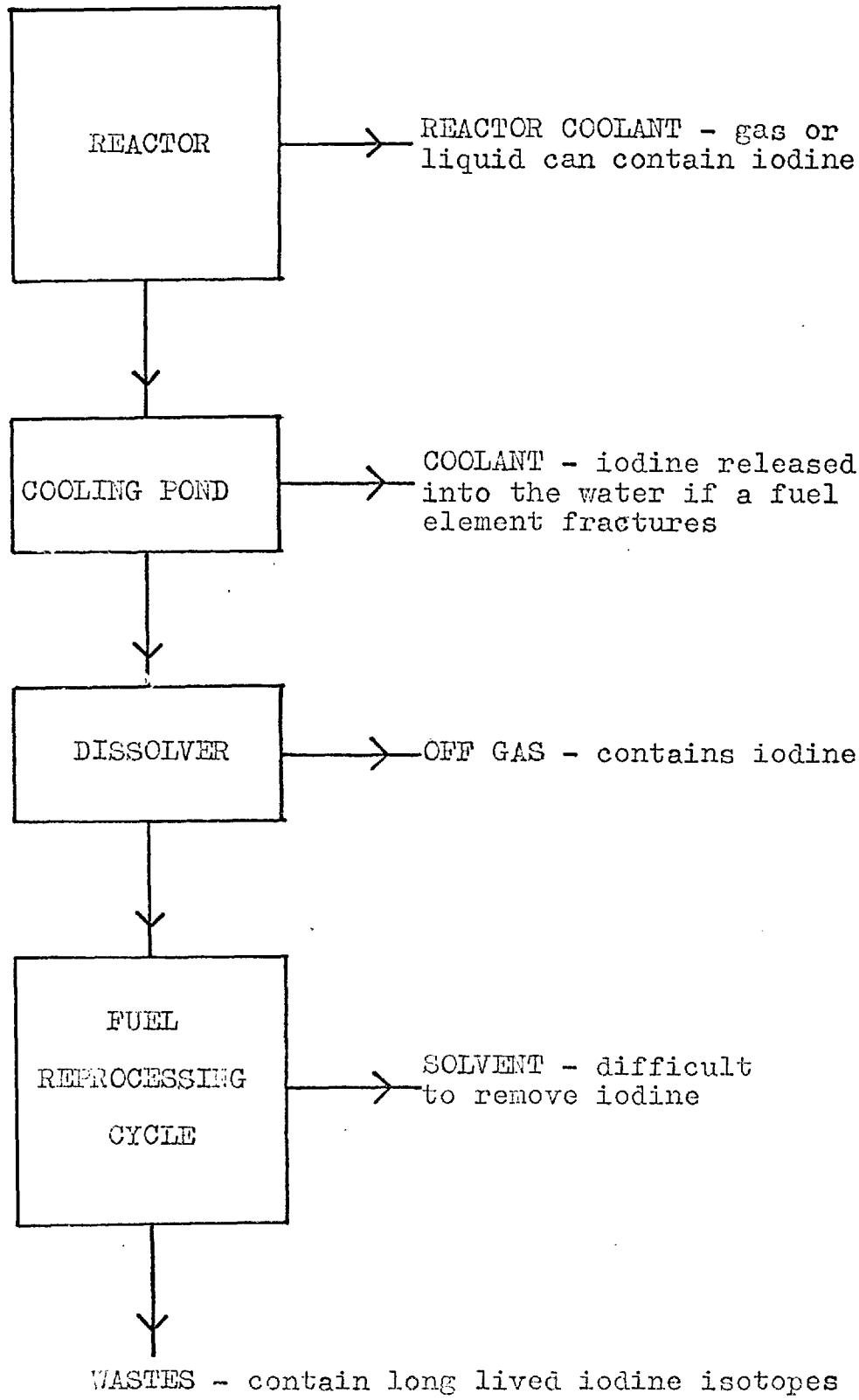
FAST FISSION YIELD OF IODINE FROM PLUTONIUM-239

ISOTOPE	HALF LIFE	COOLING PERIOD AFTER 135 DAY IRRADIATION (DAYS)				
		0	30	60	100	365
I^{127}	stable	0.582	0.565	0.574	0.584	0.613
I^{129}	1.7×10^{7} y.	1.800	1.800	1.800	1.800	1.800
I^{131}	8.0 d	0.420	0.031	0.002	-	-
I^{133}	20.8 h.	0.059	-	-	-	-

Yields expressed as atoms/100 atoms fissioned.

FIGURE 1.1

IODINE CONTAMINATION IN NUCLEAR TECHNOLOGY



ANALYTICAL METHODS

SECTION TWO

2. ANALYTICAL METHODS

2.1. INTRODUCTION

A wide variety of analytical techniques exist for the estimation of iodine in solution. The following have been suggested:-

(i) Iodometry (106) - a simple method based on volumetric estimation by titration.

(ii) Spectrophotometry (134, 107) - useful for the estimation of iodine as the tri-iodide (I_3^-), also for the detection of other iodine species.

(iii) Radioactive techniques - activation analysis (110-114) and tracer studies have a wide application in the estimation of iodine.

(iv) Spark excitation methods - these methods have been suggested as suitable for analysing iodine solutions (118, 119).

(i) - (iii) were used in this study. (iv) was rejected as being too cumbersome and inaccurate. A gradual evolution from iodometry to radioactive tracer techniques emerged during the research. Spectrometry was used alongside both these techniques, both for the estimation of iodine and in the detection of other iodine species. Each of these methods will be described in some detail.

2.2. Iodometry

Iodometry (106) is used for the estimation of molecular iodine in aqueous solutions. It makes use of the reaction:-

$$I_2 + 2^- \rightleftharpoons 2I^-$$

Usually the oxidation of sodium thiosulphate to tetrathionate provides the electrons required:-

$$2S_2O_3^{--} + I_2 \longrightarrow S_4O_6^{--} + 2I^-$$

$$1 \text{ mol } S_2O_3^{--} \equiv 1 \text{ mol } \tfrac{1}{2}[I_2]$$

Iodine in aqueous solution has an intense yellowish-brown colour and its presence can be directly detected in low concentrations ($\sim 10^{-4}$ mol.dm.$^{-3}$). However, a more pronounced colour change is obtained if starch is added to the iodine solution just before the end point. Starch reacts reversibly with iodine forming an intensely blue complex visible at low concentrations ($\sim 10^{-5}$ mol. dm.$^{-3}$ in the presence of trace iodide; above this concentration if iodide is not present).

In this work very low concentrations of iodine were used (below 10^{-3} mol.dm.$^{-3}$) and starch was not completely satisfactory as an indicator. Chloroform was chosen as a more suitable alternative (106). The iodine was extracted into the chloroform giving a deep pink colour. As the titration proceeded the iodine was back extracted into the aqueous phase so that the end point was shown when the chloroform went colourless. Iodine can be detected at a concentration of $\sim 10^{-6}$ mol.dm.$^{-3}$ by this method.

Unfortunately, this method was also not entirely satisfactory. Titrations have to be performed slowly with periodic shaking and despite the use of stoppered flasks, it is undesirable to prolong a titration due to the volatilisation of iodine. Any slight losses will lead to an erroneous result. This technique could not be used directly in nitric acid solutions because of the reaction between the acid and thiosulphate. Neutralisation of the acid before titration is complicated and can lead to further errors (133).

2.3. Spectrophotometry

Spectrophotometry (134) was used throughout the experimental work for the determination of iodine, iodide and iodate under a variety of conditions.

Iodine solutions are highly coloured and thus many colorimetric and spectrophotometric methods have been developed. Snell et al (107) have devoted a chapter to different standard estimations. The most widely used method utilises I_3^- absorbance at 352 nm.(107, 108).

A standard I_3^- solution was prepared, checked by iodometry against sodium thiosulphate solution and used to calibrate a Beckman DBG spectrophotometer. (graph 2.1). An iodine sample was then diluted to an appropriate concentration and two $cm.^3$ of a 5% potassium iodide solution was added. This converted the molecular iodine to I_3^- which was then estimated at 352 nm. in a one cm. glass cell against a water blank. From the calibration curve, the molecular iodine concentration of the sample was computed.

This method was suitable for aqueous molecular iodine solutions. However, iodide is rapidly oxidised by nitric acid to iodine. This would obviously lead to errors and a more general method was developed. This was as follows:-

(i) the diluted, acidic, iodine sample (10 $cm.^3$) was shaken with chloroform (3 $cm.^3$) in a twenty five $cm.^3$ separating funnel. The iodine was mainly extracted into the organic layer.

(ii) the heavier organic layer was run off into another separating funnel and washed with two aliquots of deionised water (10 $cm.^3$).

(iii) the iodine was then extracted from the organic layer, as I_3^-, by shaking with a 5% by weight solution of potassium iodide (5 $cm.^3$).

The I_3^- solution was then estimated at 352 nm, as before. A second calibration curve (graph 2.2) was prepared for this method in order to

allow for losses of iodine during the extraction routine. This technique was more tedious and less accurate than the previous method, but of wider applicability.

It also proved useful to calibrate the spectrophotometer for a direct estimation of molecular iodine. In solvents "inert" to iodine, (i.e. those which do not form charge transfer complexes), a peak exists at 520 nm (109) due to the presence of molecular iodine. This peak was used for the estimation of iodine in a typical inert solvent, i.e. n-heptane. A calibration curve was prepared (graph 2.3) as before, but against a n-heptane blank in one cm. glass cells. The method was considerably less sensitive than the previous estimation (table 2.1). The absorbance did not appear to obey the Beer-Lambert law at low concentrations.

A Unicam SP 700 scanning spectrophotometer was also used for the identification of iodine species in nitric acid solutions and for the investigation of iodide species in contact with the resin. These aspects of the work will be discussed in detail in the appropriate sections.

2.4. Radioactive Techniques

Two main techniques of this kind are available for the analysis of iodine, activation analysis (110-114) and tracer techniques (116, 117, 135). The two are discussed in detail below.

2.4.1. Activation Analysis

If an iodine sample is irradiated in a nuclear reactor together with a standard sample the following reaction occurs:-

$$^{127}I\ (n,\gamma)\ ^{128}I \quad \text{capture cross section} = 6.3 \times 10^{-28}\ m^2$$

Only iodine-128 is formed in this reaction since iodine is monoisotopic. This iodine-128 decays principally by β,γ emission with a half life of

twenty five minutes (120). By comparing the activity of the sample and of a standard, using a geiger counter, the iodine concentration in the sample can be determined.

Activation was considered for two possible uses. Firstly, as a straightforward technique for the estimation of iodine in samples taken from the experiment and secondly, it was thought feasible to use iodine-128 directly as a tracer. The latter was considered to be impractical since the short half life of iodine-128 necessitated the use of large amounts of activity. The former method was also rejected for a variety of reasons. Samples would have had to be specially prepared, since elemental iodine is volatile in aqueous solution and thus not suitable for activation. The half life is rather short bearing in mind that transport of samples from the reactor usually takes at least two hours. For these reasons it was decided to adopt a standard radioactive tracer method.

2.4.2. Radioactive Tracer Analysis

Tracer analytical methods are simple versatile and reasonably accurate. Since sophisticated counting apparatus was available these techniques were used for most routine analytical purposes.

Iodine isotopes ^{117}I - ^{140}I have been prepared. Of these, the most suitable tracers for this work were ^{125}I (60 day half life), ^{126}I (13 day half life) and ^{131}I (8 day half life). Only ^{125}I and ^{131}I are readily available and only these were considered. Both can be obtained at high specific activity and in high purity and both can be counted with equal efficiency (122). Iodine-125 is also easy to handle because of its low energy radiations compared with iodine-131, and its longer half life permits longer stockholding. Iodine-125 was therefore chosen for use. Its decay scheme is shown in fig. 2.1.

Two scintillation counting methods are considered suitable for this isotope, either using a liquid scintillant (116, 117, 135) or an activated sodium iodide crystal (116). Both of these methods will be described below.

2.4.2.a. Liquid Scintillation Counting

The counting sample in this method of analysis consists of three components; the radioactive material, an organic solvent or solvent mixture, and one or more organic phosphors. Radiation emitted by the sample material is absorbed in and its energy transferred to the solvent and thence to the phosphor which emits a burst of light photons. These photons are then absorbed by the photocathode of a photomultiplier tube which converts them into an electronic pulse. The pulse, after suitable amplification, is registered as a count corresponding to the emission of the radiation. The amount of light emitted by the phosphor depends on the energy of the incident radiation or particle. With suitable electronic equipment (in this case an anti-coincidence counting head, linked to a Harwell 2000 series unit) it is possible to distinguish between radiations of different energies. With a single photomultiplier tube a high background count is obtained due to spurious electron cascades in the tube. This effect can be reduced by "anti-coincidence" counting. Two photomultipliers are used so that emitted light from the phosphor is detected simultaneously in both photomultipliers and a simultaneous pulse arises from both. This is then amplified and registered. Spurious pulses arising within the photomultiplier tubes will not generally coincide and hence will be rejected by the counter.

Three scintillant mixtures were tested. These were selected for their tolerance to aqueous samples, their compositions were:

Mixture one - Triton X-100 2 parts: Toluene - 0.4%
PPO 1 part.

Mixture two - Triton X-100 1 part : Toluene - 0.4%
PPO 2 parts.

Mixture three - NE-220, a scintillant manufactured by Nuclear Enterprises Ltd.

Triton X-100 is a proprietary name for an isoctyl phenoxy polyethoxy ethanol containing some ethylene oxide (136); PPO is 2,5-diphenyloxazole.

Mixtures one and two were miscible with up to about 25 v/o water whilst mixture three could contain a maximum of about 10 v/o.

In order to calibrate the liquid scintillation counter, energy scans were carried out for each scintillant. (graphs 2.4 to 2.7). For a given amplification, a thin window of energy was used. The countrate in this window was determined over a wide energy range. The experiment was repeated for a series of amplifications. The radioactive sample used for these scans was iodine-125 labelled, carrier free, aqueous potassium iodide solution. A 1.25 $cm.^3$ sample was used, diluted to 10 $cm.^3$ for mixtures one and two, and a 0.5 $cm.^3$ sample diluted to 10 $cm.^3$ was used for mixture three. The optimum counting conditions for the mixtures are compared in table 2.2.

Two criteria are of major importance in considering the performance of liquid scintillants in aqueous solutions. Firstly, the aqueous tolerance of the scintillant and secondly the countrate obtained for a given activity. These two factors can be expressed as two countrates, i.e. the countrate per $cm.^3$ of scintillant and the countrate per $cm.^3$ of the standard active solution. (Table 2.2.) Mixture two proved to be the most efficient by the first criteria, mixture three by the second. It therefore appears that the choice of scintillants depends on the nature of the experiment. For an experiment where there is low activity present, mixture two proves the

better choice. More generally, and in particular for more active samples, mixture three appears to be the more suitable. Also it proved possible to resolve both main iodine-125 energy peaks with mixture three.

2.4.2.b. Activated Sodium Iodide Crystal Counting

Despite the fact that Rhodes (116) has suggested that liquid scintillation counting is more advantageous than sodium iodide crystal γ-spectrometry, the latter was also tested.

A well crystal of thallium activated sodium iodide was available. This was encased in aluminium alloy which made it suitable for counting low energy radiation.

A phosphor of this type, on receiving radiation, emits a light pulse. These pulses are absorbed by a photoelectric cell, the resultant electronic pulse is amplified by a photomultiplier tube, and is then registered as an event by an electronic counter. The light output from the phosphor is proportional to the energy absorbed by the crystal. This means that given a suitable standard source, the energy of the radiation emitted by the crystal sample can be determined. One of the disadvantages of this technique is that the background count rate is usually high due to the absorbance of cosmic radiation. In the experimental work this was reduced by a factor of four by using a two inch thick lead shield around the counter.

A one cm^3 sample of labelled potassium iodide was placed in a polythene capped sample tube. A window of 0.05 volts was used and scanning started at a threshold value of 0.15 volts. This meant that after amplificiation, the counter displayed all counts received in the energy range corresponding to 0.15 - 0.20 volts. The countrate was determined in this way over the threshold range 0.15 - 1.5 volts for various levels of amplification. These scans are shown in graphs 2.8, 2.9 and 2.10. A threshold of 0.15 volts with

a window of 0.3 volts, at a gain of 50 dB, was selected in order to count over the low energy iodine-125 peak only. This kept the background low and as can be seen from the energy scans, the low energy peak contains the majority of counts. The actual arrangement of sample and counter is shown in figure 2.2.

2.4.2.c. Comparison of the Counting Methods

In order to compare the counting methods a relative efficiency was defined, as

$$= \frac{\text{observed countrate per cm}^3 \text{ of standard solution}}{\text{countrate obtained on the NaI crystal per cm}^3 \text{ of standard solution}}$$

Using this definition the relative efficiency of the well crystal is 100%. Relative efficiencies and background counts are compared in table 2.3. It can be seen that the sodium iodide method was considerably more efficient than the corresponding liquid scintillation methods, although the background was slightly higher. Also the spectrum shape, i.e. the resolution was much better with the sodium iodide crystal, and furthermore, the sample could be in any liquid form (acid, aqueous or organic). With the scintillant mixtures the amount of aqueous solution and the acidity of the solution ~~was~~ were limited.

It can be seen, therefore, that the sodium iodide well crystal technique proved in this case to be better in most respects and had only a slightly higher background. This method was consequently adopted as the most suitable analytical technique for most of the experimental work. The linearity of this method is illustrated by graph 2.11.

Some further radioactive work was carried out in order to elucidate the decay scheme of iodine-125 and to determine the energies of the radiations counted. Details of this work are given in appendix one.

TABLE 2.1

MOLAR DECADIC ABSORBTIVITIES OF I_3^- AND I_2

METHOD OF DETERMINATION	MOLAR DECADIC ABSORBTIVITY 10^{+8} m^2. $mol.^{-1}$
IN AQUEOUS SOLUTION $[I_3^-]$ ESTIMATED AT 352 nm.	23
IN ACID SOLUTION FOLLOWED BY SOLVENT EXTRACTION INTO AQUEOUS SOLUTION, $[I_3^-]$ ESTIMATED AT 352 nm.	13
IN n-HEPTANE SOLUTION $[I_2]$ ESTIMATED AT 520 nm.	0.9

TABLE 2.2

COMPARISON OF SCINTILLANTS FOR IODINE-125 DETERMINATION

VOLUME OF SAMPLE	COUNTING CONDITIONS	BACKGROUND cps	COUNTRATE cps
0.5 cm^3 potassium iodide-125 solution.	10 cm^3 scintillant "NE-220" Gain 58 dB. Threshold 0.15 v.	1.59	5139
1.25 cm^3 potassium iodide-125 solution. Activity per cm^3 same as above	10 cm^3 scintillant 2 parts Triton X 100: 1 part Toluene PPO Gain 44 dB. Threshold 0.15 v.	1.47	4972
1.25 cm^3 potassium iodide-125 solution. Activity as above	10 cm^3 scintillant 1 part Triton X 100: 2 parts Toluene PPO Gain 44 dB. Threshold 0.15 v.	1.47	7992

TABLE 2.3

COMPARISON OF COUNTING METHODS

METHOD	BACKGROUND c.p.s.	RELATIVE EFFICIENCIES
Sodium Iodide Well Crystal	1.95	100%
NE - 220	1.59	89.8%
2 parts Triton X-100 : 1 part Toluene PPO	1.47	43.4%
1 part Triton X-100 : 2 parts Toluene PPO	1.47	69.8%

FIGURE 2.1

DECAY SCHEME OF IODINE-125

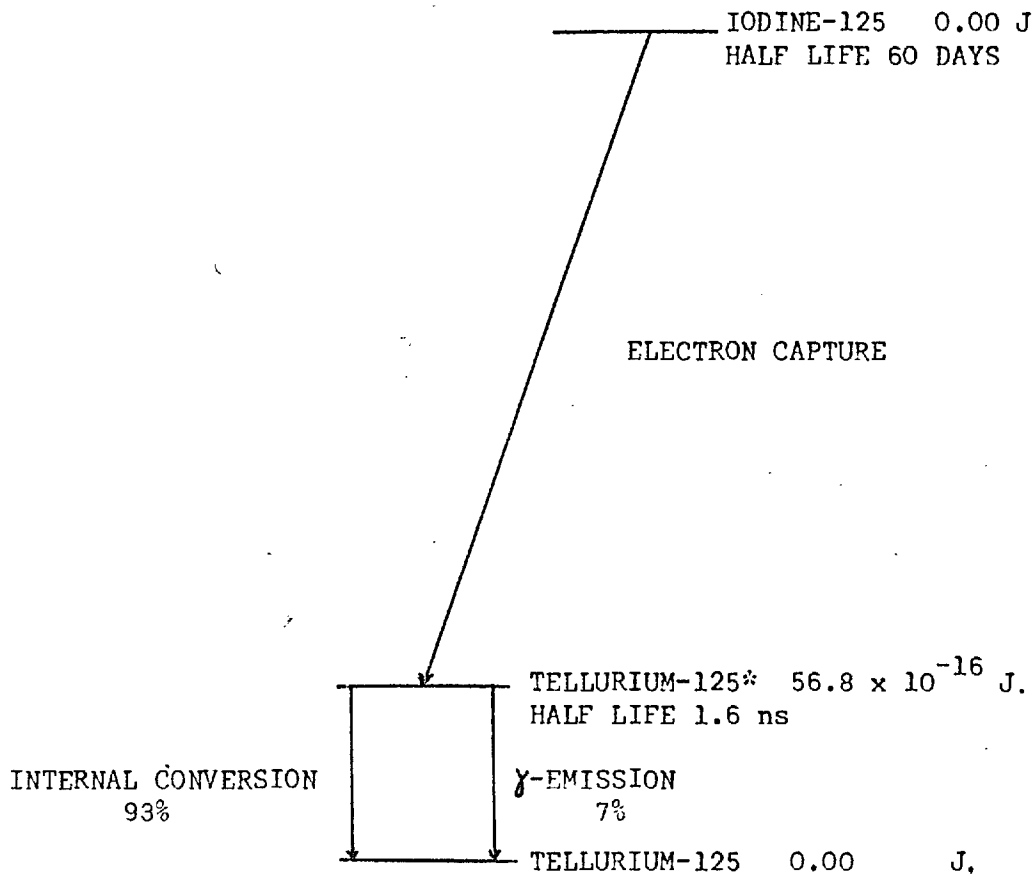
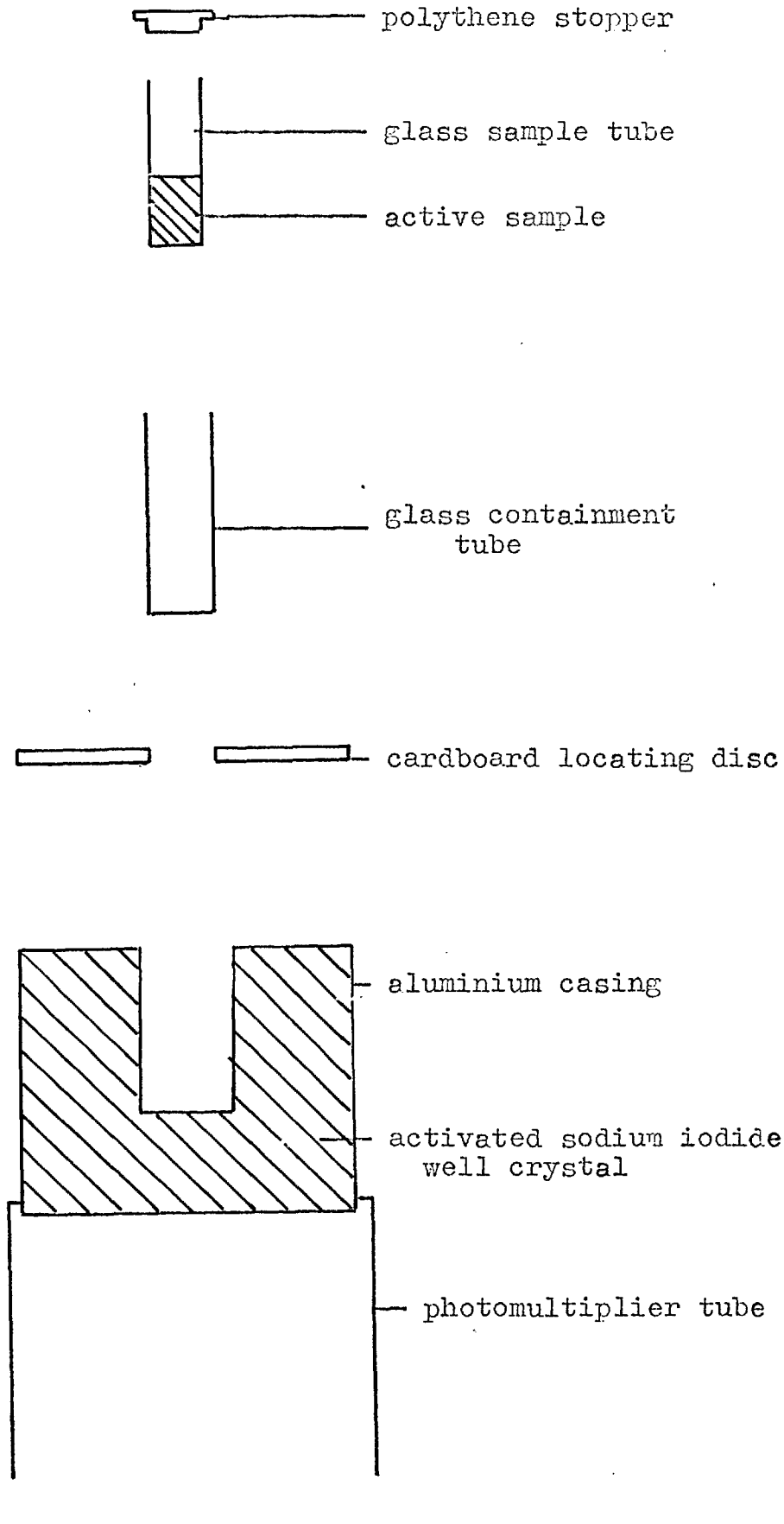


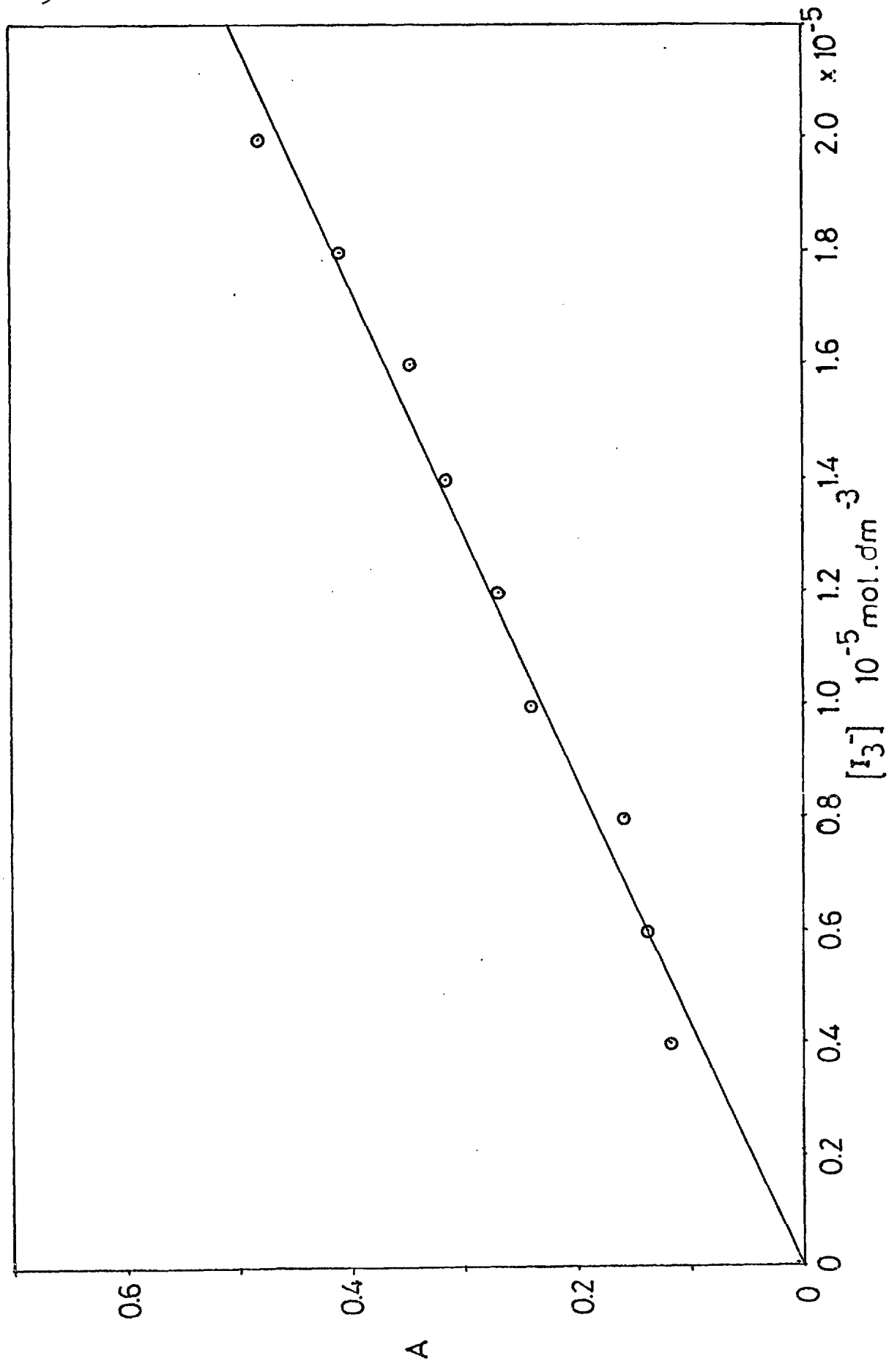
FIGURE 2.2

EXPLODED VIEW OF THE COUNTING ARRANGEMENT



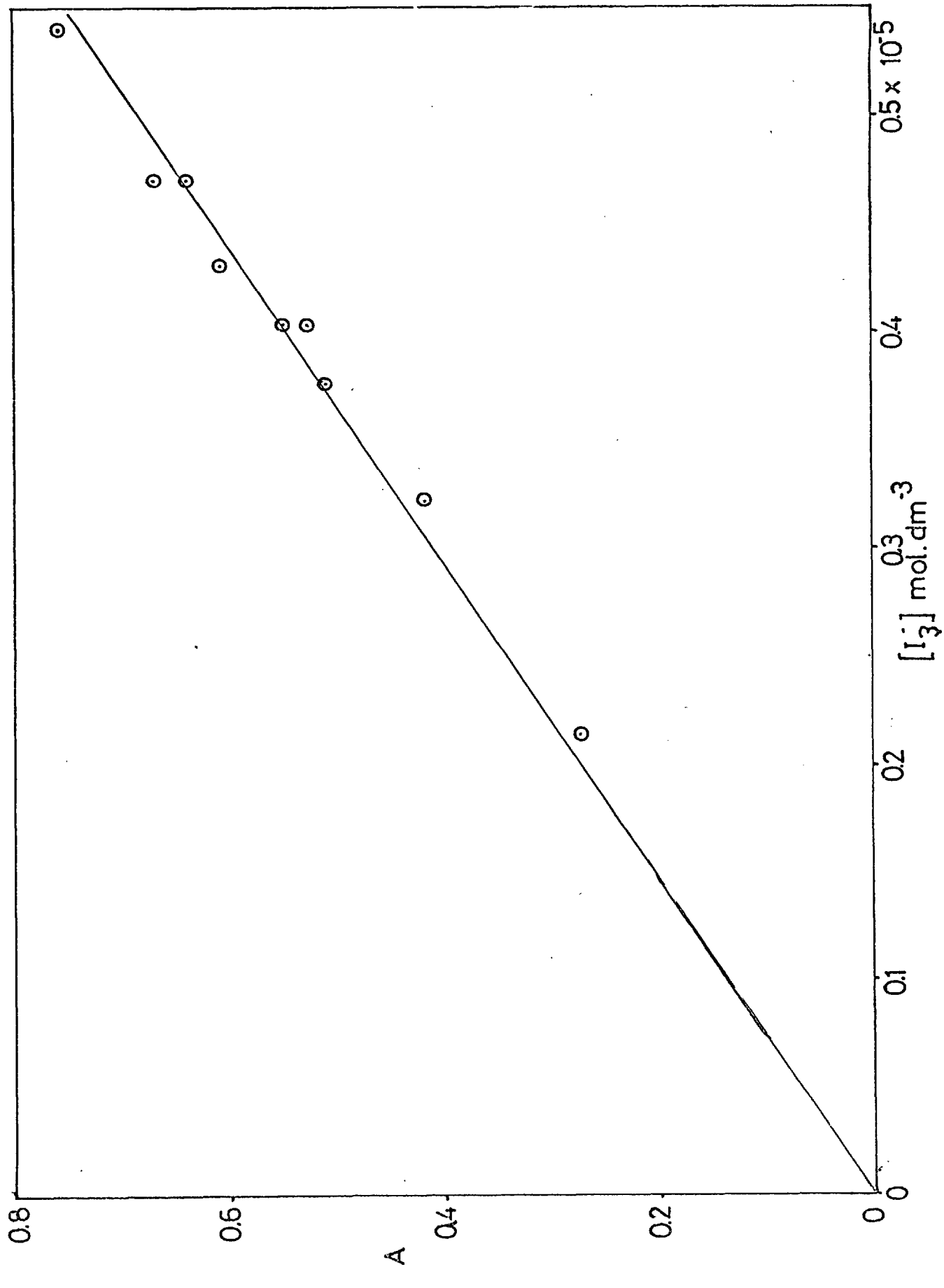
GRAPH 2.1

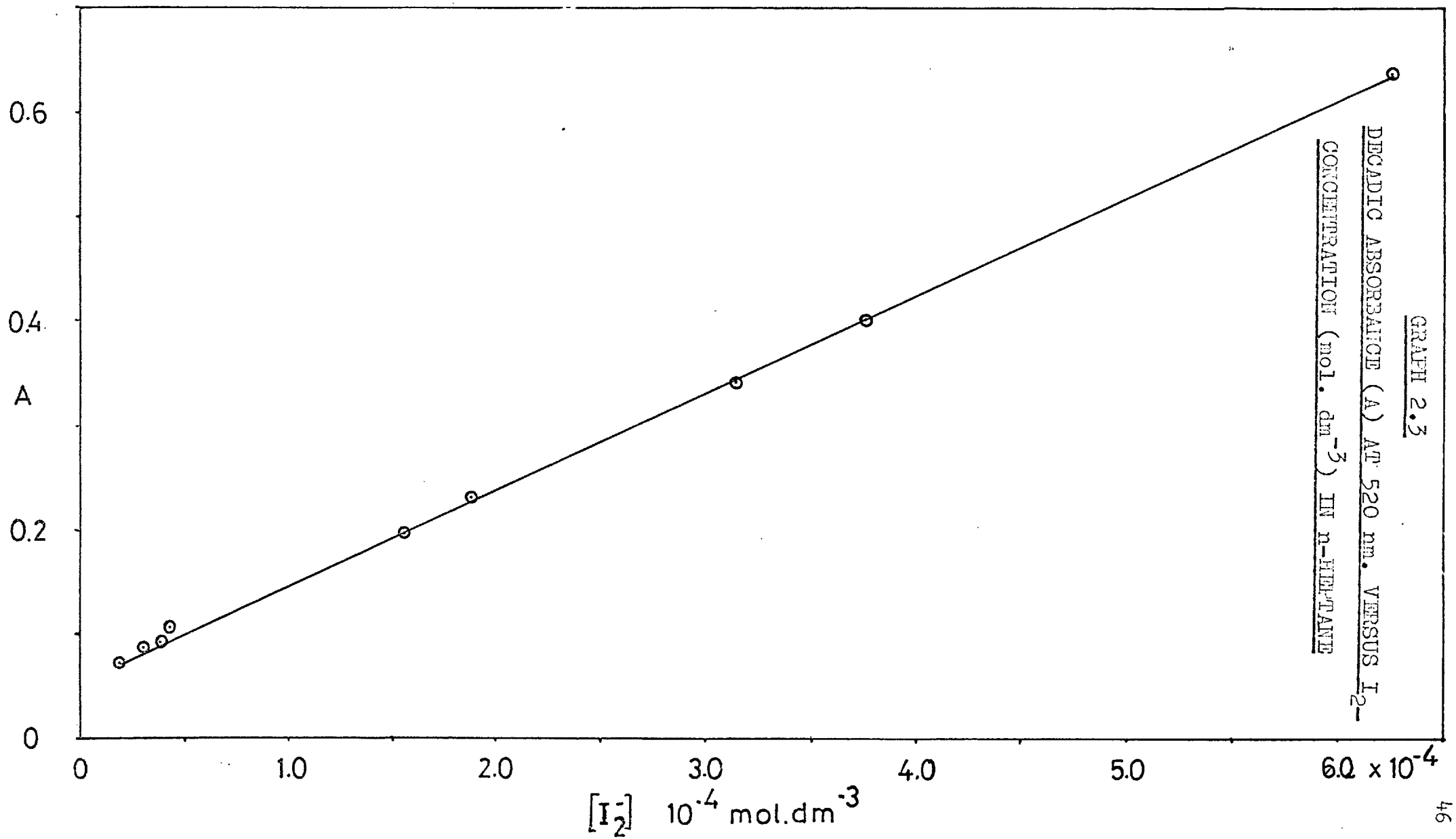
DECADIC ABSORBANCE (A) AT 352nm, VERSUS I_3^- CONCENTRATION (I_3^- mol. dm^{-3}) FROM AQUEOUS SOLUTIONS



GRAPH 2.2

DECADIC ABSORBANCE (A) AT 352 nm. VERSUS I_3^- CONCENTRATION (I_3^- mol. dm^{-3}) FROM ACID SOLUTIONS



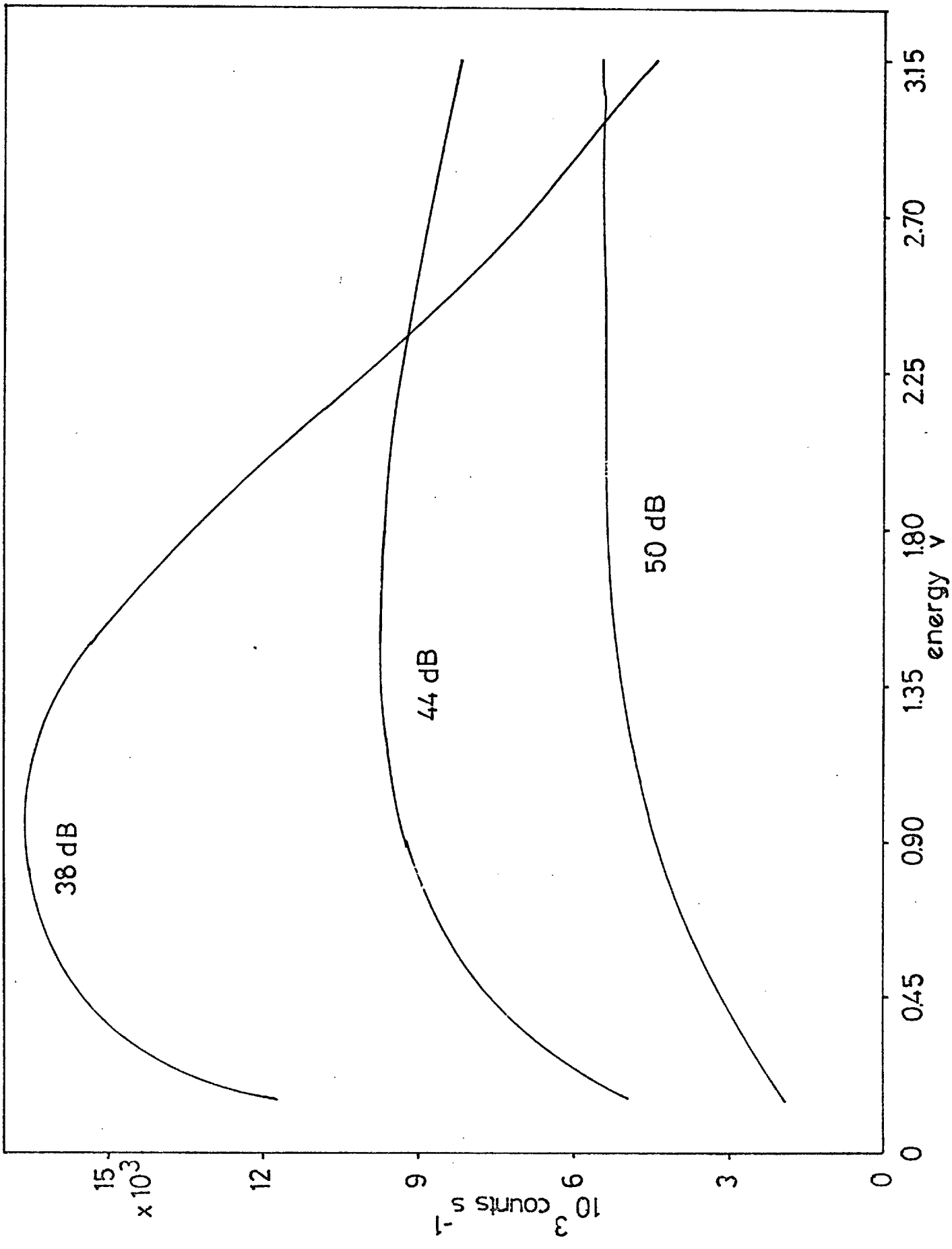


GRAPH 2.3

DECADIC ABSORBANCE (A) AT 520 nm. VERSUS I_2^- CONCENTRATION (mol. dm^{-3}) IN n-HEPTANE

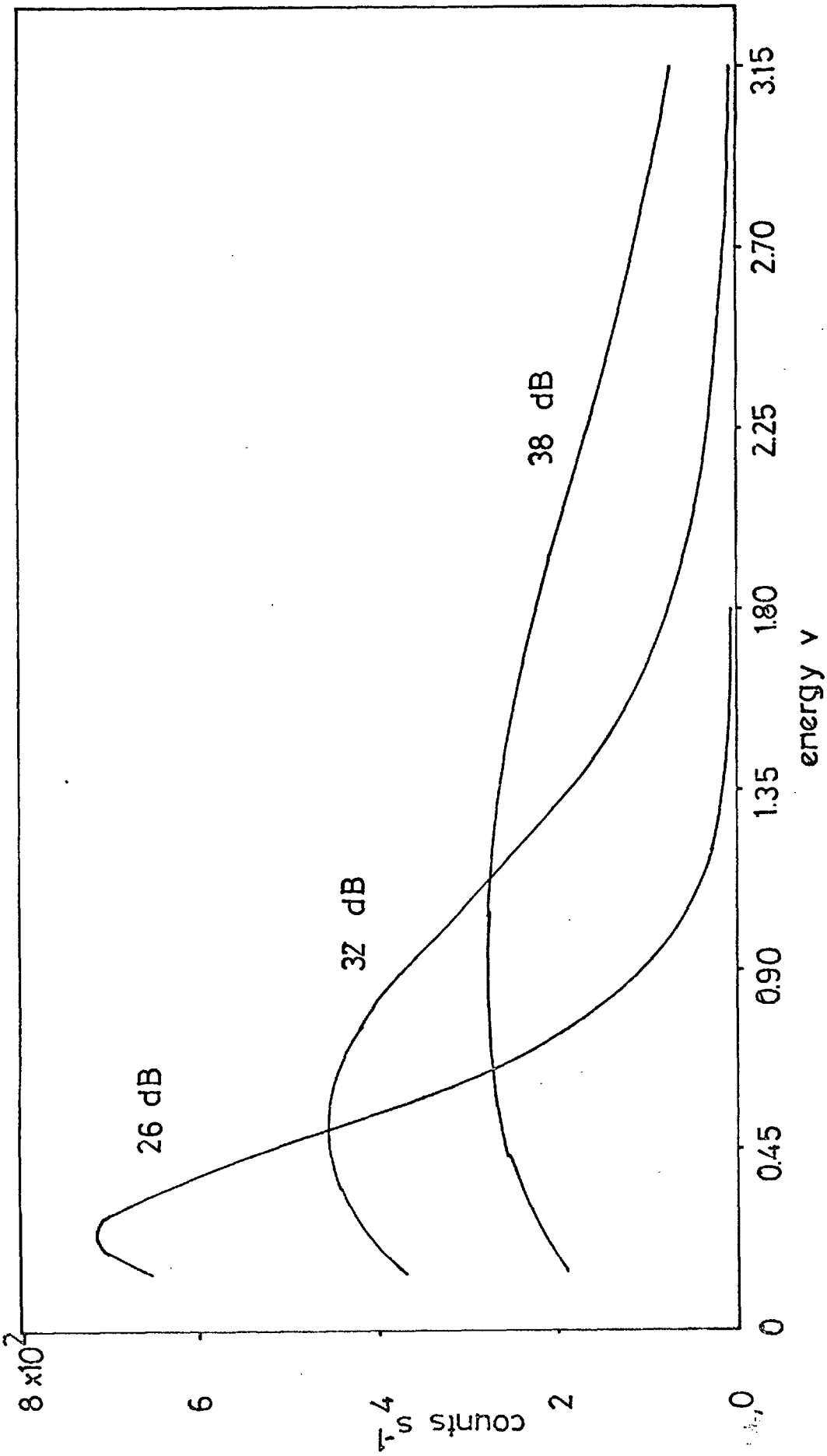
GRAPH 2.4

COUNTRATE VERSUS THRESHOLD VOLTAGE FOR TRITON X-100 (1 part):TOLUENE -PPO (2 parts) AT VARIOUS GAINS



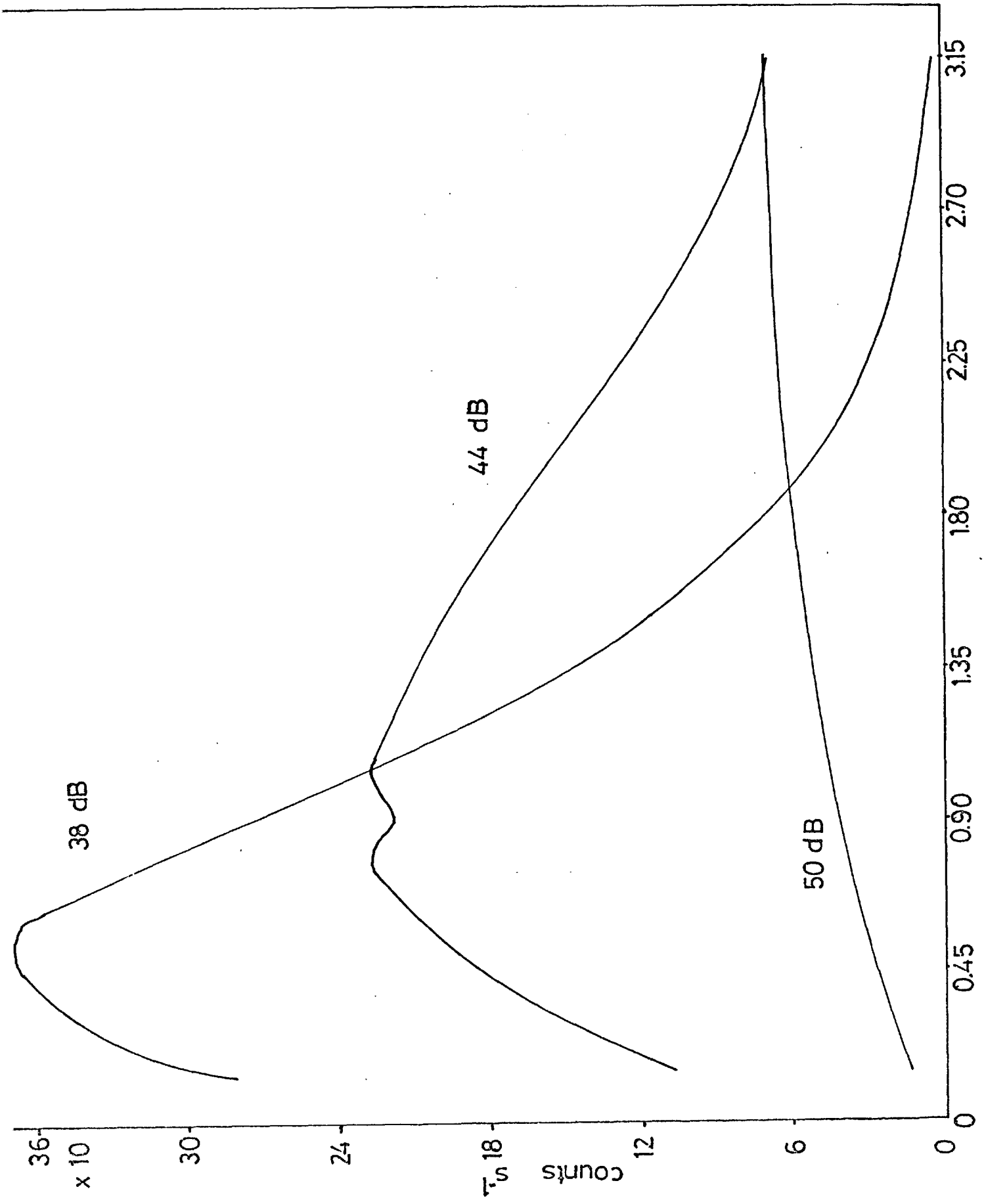
GRAPH 2.5

COUNTRATE (s^{-1}) VERSUS THRESHOLD (v_s) FOR TRITON X-100 (1 part): TOLUENE -PPO (2 parts) AT VARIOUS GAINS



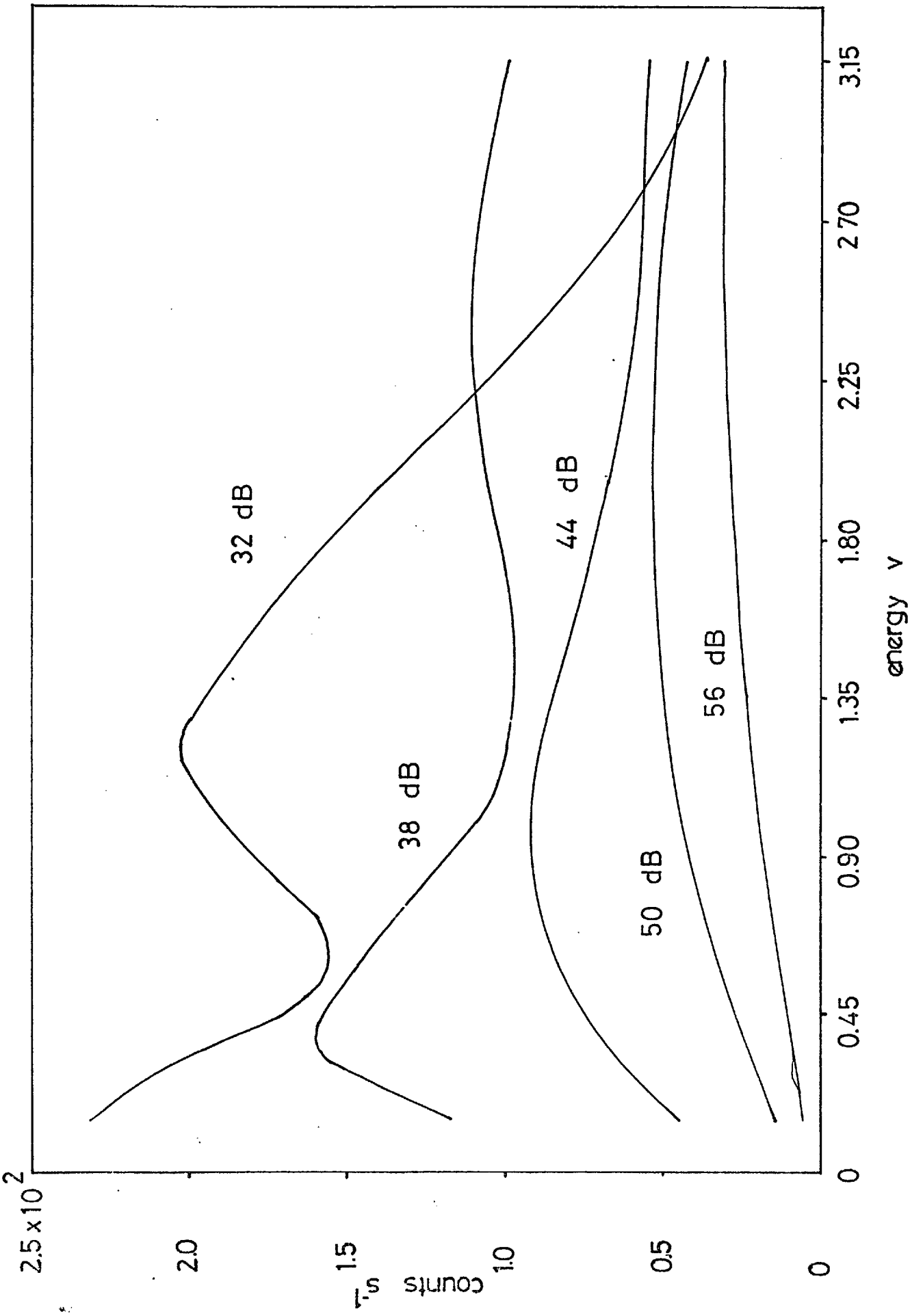
GRAPH 2.6

COUNTRATE (s^{-1}) VERSUS THRESHOLD (v) FOR TRITON X-100 (2 parts): TOLUENE -PPO (1 part) AT VARIOUS GAINS



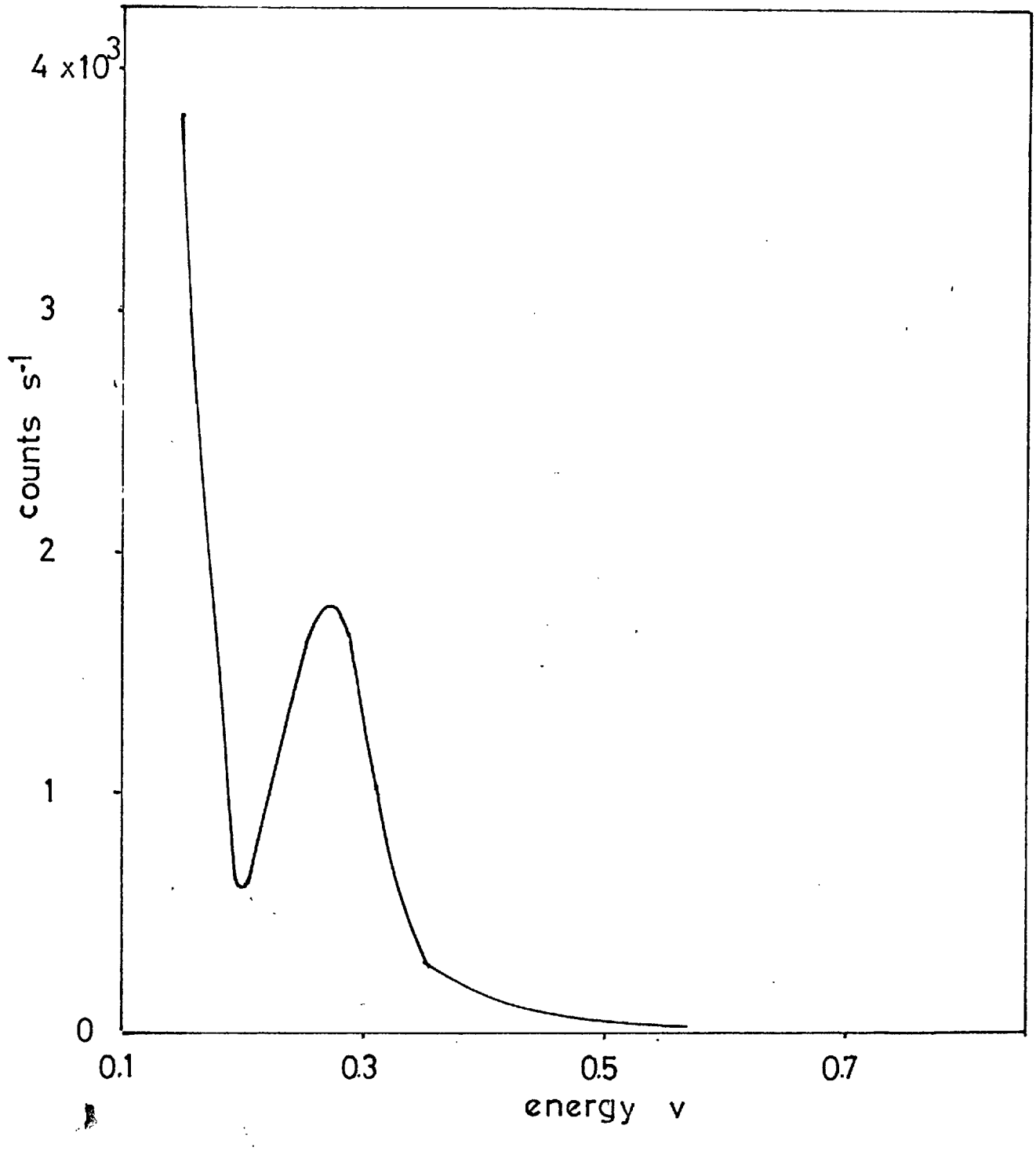
GRAPH 2.7

COUNTRATE (s^{-1}) VERSUS THRESHOLD (v) FOR NE-220 SCINTILLANT AT VARIOUS GAINS



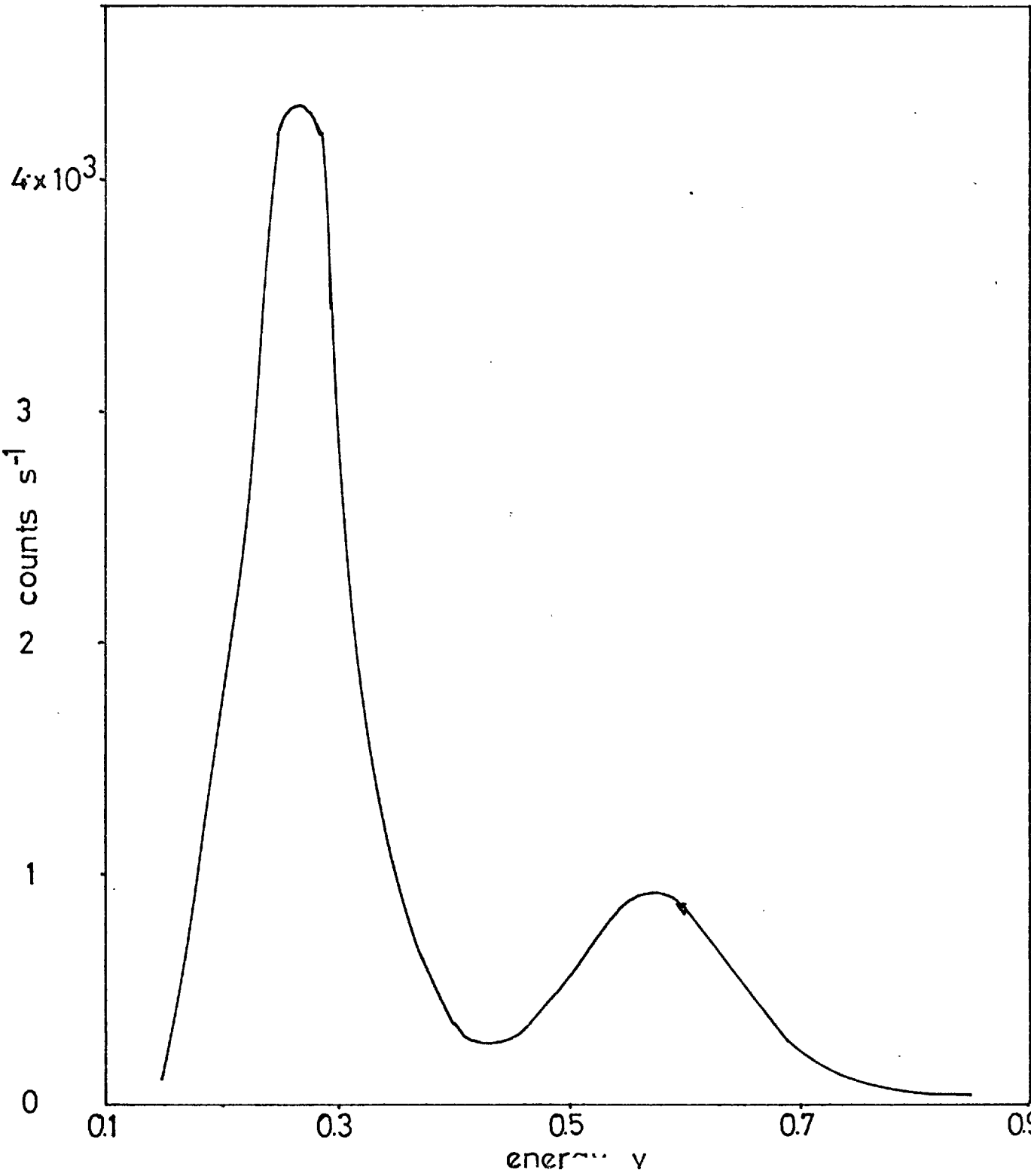
GRAPH 2.8

COUNTRATE (s^{-1}) VERSUS THRESHOLD (v) FOR A SODIUM IODIDE WELL CRYSTAL COUNTER AT A GAIN OF 44 dB



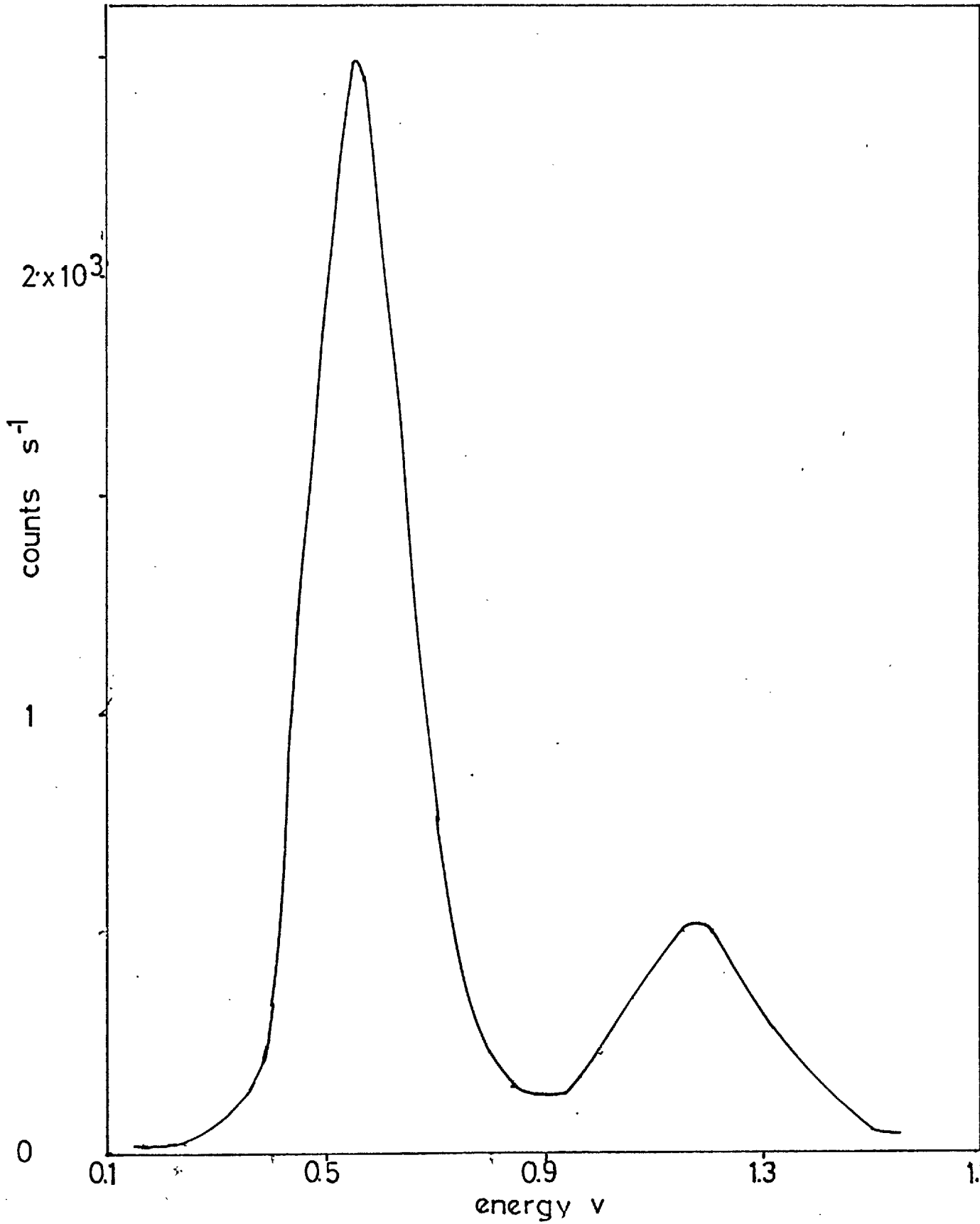
GRAPH 2.9

COUNTRATE (s^{-1}) VARSUS THRESHOLD (v) FOR A SODIUM IODIDE WELL CRYSTAL COUNTER AT A GAIN OF 50 dB



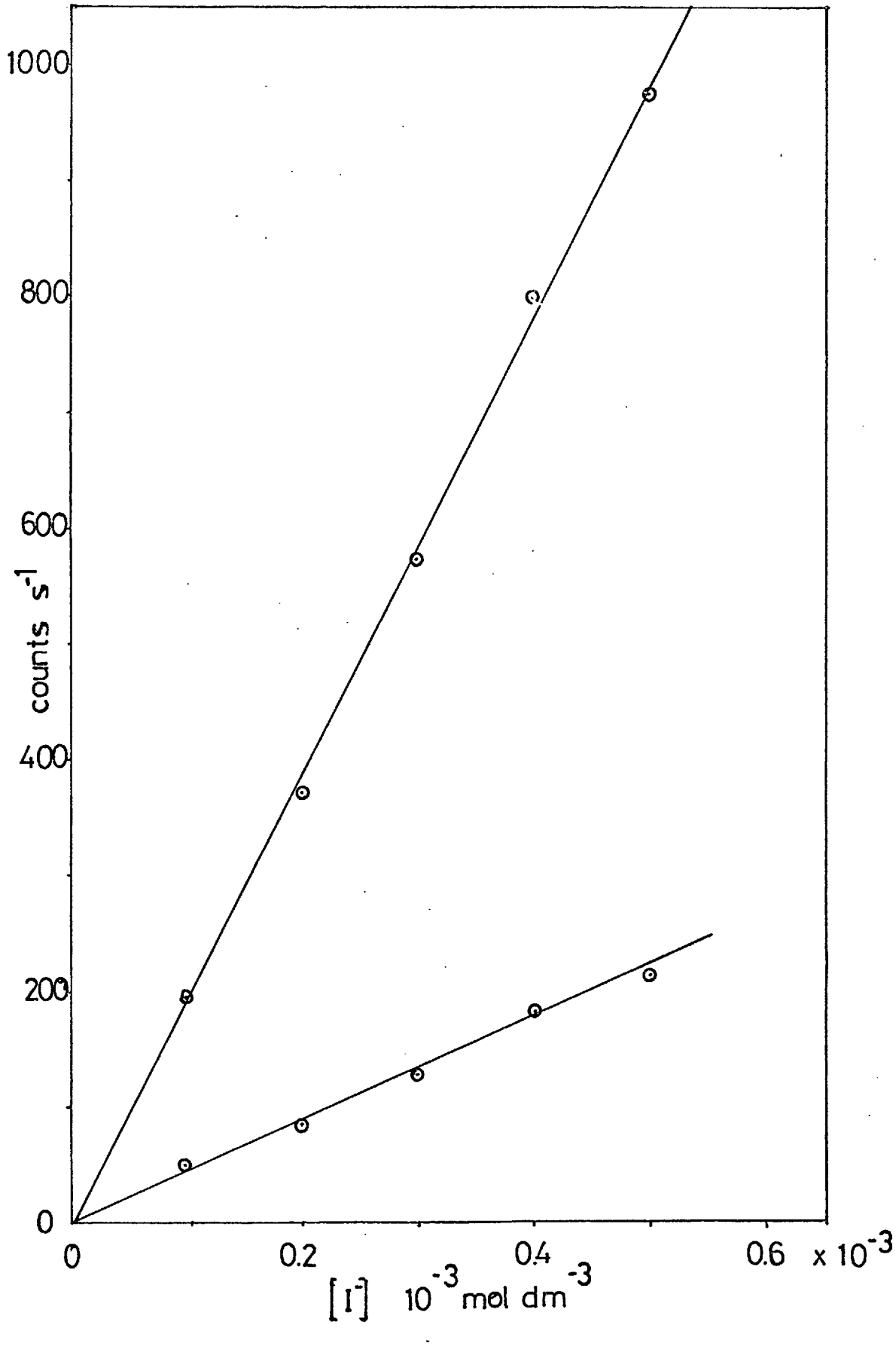
GRAPH 2.10

COUNTRATE (s^{-1}) VERSUS (v) FOR A SODIUM IODIDE WELL CRYSTAL COUNTER AT A GAIN OF 56 dB



GRAPH 2.11

COUNTRATE (s^{-1}) VERSUS IODIDE CONCENTRATION, SHOWING THE LINEARALITY OF THE ANALYTICAL METHOD FOR BOTH IODIDE PEAKS ON THE SODIUM IODIDE WELL CRYSTAL



ADSORPTION AND ION EXCHANGE

SECTION THREE

3. ADSORPTION AND ION EXCHANGE

3.1. INTRODUCTION

In this section the fundamental theories of ion exchange and adsorption are discussed. In a study of the uptake of iodine from aqueous solutions both adsorption and ion exchange may play a part. A description of the types of ion exchange resin used in this work is also included for completeness.

3.2. ION EXCHANGE

Ion exchange resins are insoluble solid materials, usually crosslinked polyelectrolytes, which carry exchangeable cations or anions. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign when the ion exchanger is in contact with an electrolyte solution (140). If the exchangeable ions are cations the resin is known as a cation exchanger, if the ions are anions the resin is known as an anion exchanger.

Ion exchange and adsorption are similar; to the extent that in both cases a dissolved component can be removed from an aqueous solution into the solid phase. Ion exchange, however, is a stoichiometric process and involves the exchange of charged species in which electroneutrality is preserved. Adsorption is not necessarily stoichiometric and is not normally accompanied by the desorption of one species during the adsorption of another.

It can be seen, therefore, that the uptake of molecular iodine from an aqueous solution is not a typical ion exchange reaction, despite the fact that an ion exchange resin is used. If, however, the uptake of iodine is accompanied by the transformation of the iodine into an ionic species, ion exchange can then occur. This essentially is the problem under investi-

gation.

The most widely used, and hence the most important, ion exchange resins are organic materials. Their framework consists of an irregular, macromolecular, three dimensional network of hydrocarbon chains. The matrix carries ionic functional groups which are responsible for the ion exchange properties of the resins. For example, sulphonated polystyrene based resins contain sulphonate groups which carry the exchangeable counter ions, i.e. hydrogen in this case:-

$$R.SO_3^-H^+ + Na^+Cl^- \rightleftharpoons R.SO_3^-Na^+ + H^+Cl^- \qquad (1)$$

The hydrogen ions being exchanged for sodium ions.

Linear hydrocarbons containing ionic groups such as $-SO_3^-H^+$ are generally soluble in water. In order to render ion exchange resins insoluble in aqueous solutions, it is necessary to introduce crosslinks between the hydrocarbon chains. A cross linking agent (e.g. divinylbenzene) is added to the mixture during the resin bead manufacture. Resin beads cannot be soluble in a solvent unless carbon-carbon bonds are ruptured, but they will absorb solvents leading to a swelling of the elastic matrix. The amount of swelling which is possible for a bead depends on the quantity of crosslinking agent added during the manufacturing process. The more highly crosslinked the resin the less swelling is possible. Consequently the mobility of counter ions will be less in more highly crosslinked resins.

3.2.1. Equilibrium in Ion Exchange

A number of "equilibrium constants" have been defined for the exchange of species B for species A. Typical definitions are (166):-

(i) Separation factor α_B^A is defined by

$$\alpha_B^A \equiv \frac{[\bar{A}][B]}{[\bar{B}][A]} \qquad (2)$$

where the overbar denotes resin phase species.

(ii) Selectivity coefficient K_B^A is defined by

$$K_B^A = \frac{[\bar{A}]^{Z_B}[A]^{Z_A}}{[\bar{B}]^{Z_A}[A]^{Z_B}} \qquad (3)$$

where $|Z_I|$ represents the absolute value of the ionic valency.

Other equilibrium parameter definitions are also used (166).

3.2.2. Kinetics in Ion Exchange (167)

The rate of ion exchange is determined by a diffusion processes. The rate determining step is the diffusion of counter ions within the ion exchanger (particle diffusion) or within the liquid "film" around the exchanger (film diffusion). In an ideal system, involving the counter diffusion of exchanging ions, the Nernst-Plank equation may be used,

$$J_i = (J_i)\,\text{diff} + (J_i)e\ell = -D_i(\text{grad } C_i + z_i C_i \frac{F}{RT} \text{grad } \phi) \qquad (7)$$

where J = flux

D_i = a diffusion constant

C_i = concentration

z_i = electrochemical valence

F = Faraday constant

R = gas constant

T = absolute temperature

ϕ = electric potential

This equation has been solved under certain conditions. Since the mathematical solutions are usually complex, a whole series of empirical and simplified rate laws have been developed (168). These have been found adequate in the restricted cases for which they were devised, but often a slight alteration in conditions will invalidate such an approach.

3.3. ADSORPTION

Adsorption of iodine species is important whenever molecular iodine is present. Sorption, in general, will depend on London interactions; the dipole-dipole interaction; the relative stability of the solute inside and outside the sorbent; the volume of the swollen sorbent; the equilibrium concentration of the solute in the external solution, and temperature (72). There may, of course, be other specific interactions. A sorption study involves three substances; the sorbent, the solvent and the solute. For the sorbent there are many variables (e.g. for an ion exchange resin these include matrix structure; the degree of crosslinking; the type and acid or base strength of the ionogenic group; the charge, shape, size and hydration of the counter ions). The solvent may be aqueous, mixed or organic; polar or non-polar; other variables can include dielectric constant and solvating power. For the solute, the variables may include shape, size, polarity and relative solubility in the medium inside and outside the sorbent. The overall process of sorption is complex and there are many available theoretical approaches (74-82).

3.3.1. Equilibrium in Sorption Studies

The most widely used equilibrium isotherms in sorption theory are those of Freundlich (83), and Brunauer, Emmett and Teller (84) (which for monolayer coverage includes the Langmuir isotherm (85)).

The modified B.E.T. equation is:-

$$\frac{x}{x_m} = \frac{k(p/p_o)}{(1 - p/p_o)} \frac{(1 - (n + 1)(p/p_o)^n + n(p/p_o)^{n+1})}{(1 + (k - 1)(p/p_o) - k(p/p_o)^{n+1})} \qquad (8)$$

x_m = monolayer capacity

x = mass of adsorbate

p = pressure

p_o = saturated vapour pressure

k = constant

n = number of monolayers.

For $n = 1$, the above equation reduces to the Langmuir isotherm, i.e.

$$\frac{x}{x_m} = \frac{k(p/p_o)}{(1 - p/p_o)} \frac{(1 - 2p/p_o + (p/p_o)^2)}{(1 + (k - 1)(p/p_o) - k(p/p_o)^2)} \qquad (9)$$

Eq. (9) becomes

$$\frac{x}{x_m} = \frac{k(p/p_o)}{(1 - p/p_o)} \frac{(1 - p/p_o)^2}{(1 - p/p_o)(1 + k(p/p_o))} \qquad (10)$$

$$\frac{x}{x_m} = \frac{k(p/p_o)}{1 + k(p/p_o)} \qquad (11)$$

Equation (11) is the Langmuir isotherm. Based on these equations are other isotherms which take into account dissociation, competitive adsorption etc. (169). The above equations can be applied to solution studies by changing

the pressure ratio terms to concentrations.

Adsorption from solution, however, usually departs considerably from the ideal behaviour as represented by the Langmuir isotherm. The most widely used adsorption isotherm is empirical and was postulated by Freundlich (83):-

$$\frac{\bar{x}}{\bar{m}} = \alpha C^{1/n} \qquad (12)$$

$\bar{x}$ = mass of adsorbate

$\bar{m}$ = mass of adsorbent

C = equilibrium concentration in the solvent phase (a pressure term may be used for gaseous adsorption).

α,n = constants.

This equation has been used in the study of iodine adsorption from solution (86).

3.3.2. Kinetic Studies of Sorption

Kinetic studies of sorption have been confined to particular cases where an empirical relationship has been fitted to experimental data. However, some efforts have been made to derive more generally applicable equations. These equations have been applied to both ion exchange and sorption (129-132). Several approaches will be mentioned.

(i) The linear driving force equation,

$$\frac{d\theta}{dt} = k\,(1 - \theta) \qquad (13)$$

where k = a constant

$$\theta = \frac{\text{Iodine concentration on the resin at time t}}{\text{iodine concentration on the resin at equilibrium}}$$

θ therefore represents the fraction of adsorption sites occupied at time t.

Equation (13), therefore, states that the rate of adsorption is directly proportional to the fraction of unoccupied sites.

(ii) The quadratic driving force equation,

$$\frac{d\theta}{dt} = -k\left(\frac{\theta^2 - 1}{\theta}\right) \qquad (14)$$

or

$$\frac{d\theta}{dt} = -k\left(\theta - \frac{1}{\theta}\right) \qquad (15)$$

Equation (14) is a simplified version of the general rate law for ion exchange (eq. (7)).

(iii) The inverse driving force equation, derived in this work,

$$\frac{d\theta}{dt} = k\left(\frac{1}{\theta} - 1\right) \qquad (16)$$

Equation (16) states that the rate of adsorption is inversely proportional to the fraction of occupied sites.

Typical plots of equations (16) and (15) are shown on graph 3.1. Equation (13) is linear, the slope depending on the value of the constant k.

3.4. CHOICE OF ION EXCHANGE RESINS

Three types of resin were chosen for use in the experimental work. Ionac XAX resins (see below) were chosen because of their suitability for this type of work, Deacidite FF and Zeocarb 225 because they were considered representative of more commonly used resins. Gel-type polystyrene beads were also studied, since they showed the influence of a resin matrix alone.

3.4.1. Ionac XAX Resins

Most of the experimental work was carried out with Ionac XAX resins. These are known to be highly radiation resistant and also satisfactory for the uptake of plutonium (73, 128, 141) and hence would be suitable for use

within a nuclear fuel reprocessing cycle. Furthermore, they contain pyridine rings (see below). These were thought to be useful for the removal of iodine from aqueous solutions.

XAX 1283, 1284 and 1285 were used. All these resins consist of 2 methyl 5 vinyl pyridine crosslinked with divinylbenzene (D.V.B.). Pure divinylbenzene is not readily available and the commercial product consists of a mixture of divinylbenzene isomers (approximately 55%) and ethyl styrene (approximately 45%). XAX 1283 was crosslinked with 5% D.V.B., 1284 with 10% D.V.B. and 1285 with 15% D.V.B. (fig. 3.1).

This produces a weakly basic resin, on protonation

$$RN: + H^+NO_3^- \rightleftharpoons RNH^+NO_3^-$$

freely basic resin protonated resin

The nitrate may then be exchanged for any other counter ions.

3.4.2. Zeokarb 225

Zeokarb 225 was used to help with the elucidation of the mechanism of uptake of elemental iodine species from acid solutions.

The resin is a copolymer of styrene and divinyl benzene sulphonated with sulphuric or chlorosulphonic acid. (Figure 3.2). 8% Commercial grade D.V.B. is added and therefore some ethyl styrene is incorporated into the matrix.

The final resin, therefore, is a copolymer of styrene and divinylbenzene containing sulphate groups. This produces a strongly acidic resin with exchangeable cations.

3.4.3. De-Acidite FF

The strongly basic resin De-Acidite FF was also used.

This resin is produced by the quaternization of chloromethylated resins with a tertiary alkyl amine, trimethylamine (Figure 3.3).

3.4.4. Polystyrene Beads

Some work was also carried out with crosslinked polystyrene beads of different D.V.B. contents.

Crosslinked polystyrene is not able to absorb aqueous solutions and hence work was also carried out on the adsorption of molecular iodine from n-heptane solutions.

3.5. PREPARATION OF RESINS FOR EXPERIMENTAL WORK

All resins used were commercial grade and consequently had to be cleaned and sieved before use.

The cleaning process consisted of a series of washings:

(a) Deionised water.

(b) "Analar" grade acetone.

(c) "Analar" grade methanol.

(d) Deionised water.

The resin was then converted to its required ionic form, usually by washing with appropriate solutions of nitric acid.

The quantity of each wash was of the order of five volumes of wash per volume of resin. Operations were carried out in glass columns with a sintered glass disc as the resin support.

The resins were then air-dried in a desiccator and sieved. Sieve sizes were usually 14# 52 B.S. although some work was done on resins of smaller particle size.

Table 3.1 lists the properties of the various resins used.

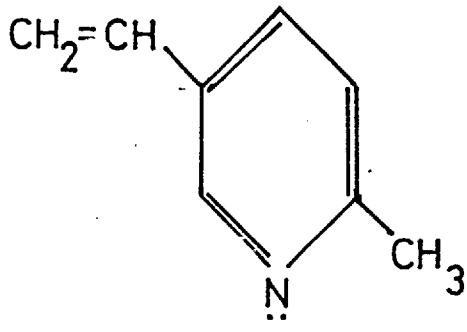
TABLE 3.1

PROPERTIES OF RESINS

Resin	Reference	Resin Capacity m mol.g.$^{-1}$ of a univalent species	Cross-linking %
XAX 1283	Coady (157)	5.3	5
XAX 1284	"	4.5	10
XAX 1285	"	4.4	15
Deacidite FF	Helfferich (158)	4.0	8
Zeocarb 225	"	4.8	8

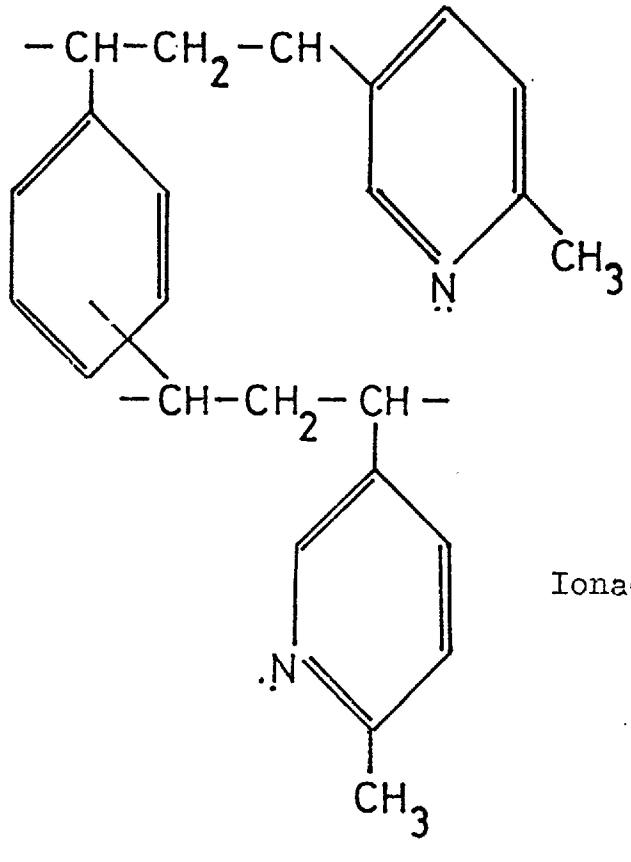
FIGURE 3.1

STRUCTURE OF IONAC XAX RESINS



2 methyl 5 vinyl pyridine

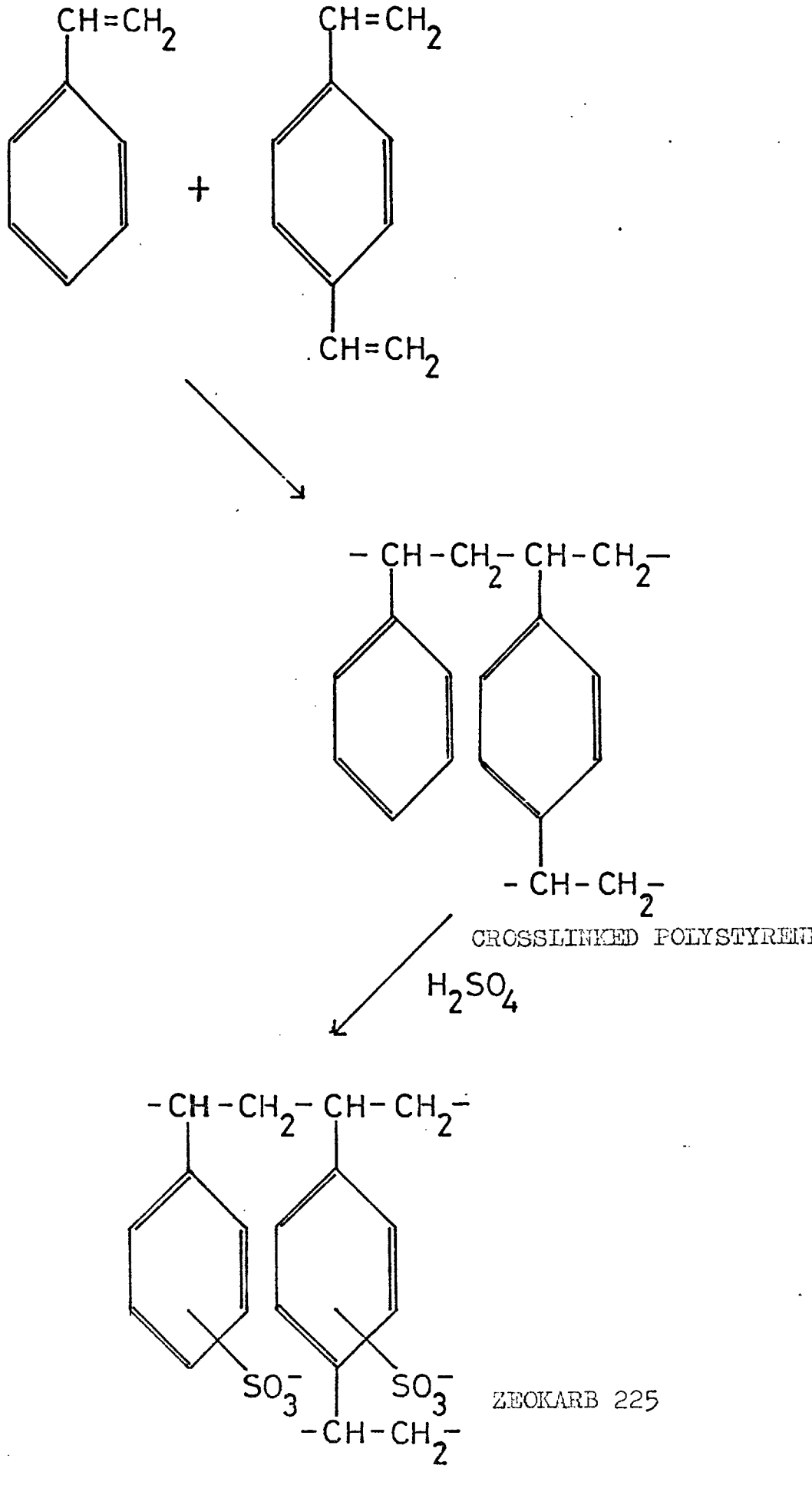
crosslinked with D.V.B.



Ionac XAX

FIGURE 3.2

STRUCTURE OF ZEOKARB 225

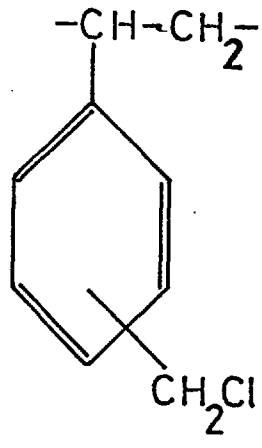


CROSSLINKED POLYSTYRENE

ZEOKARB 225

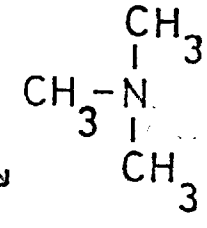
FIGURE 3.3

STRUCTURE OF DE-ACIDITE FF

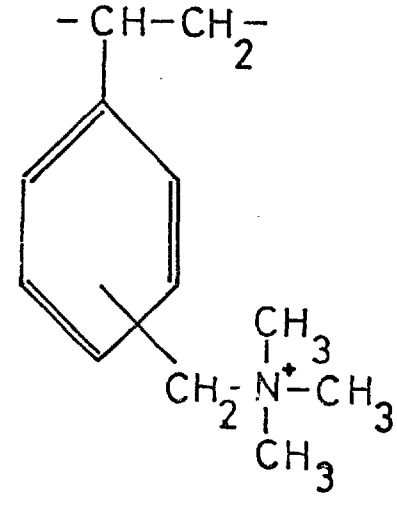


chloromethylated polystyrene

~~polyvinyl chloride~~



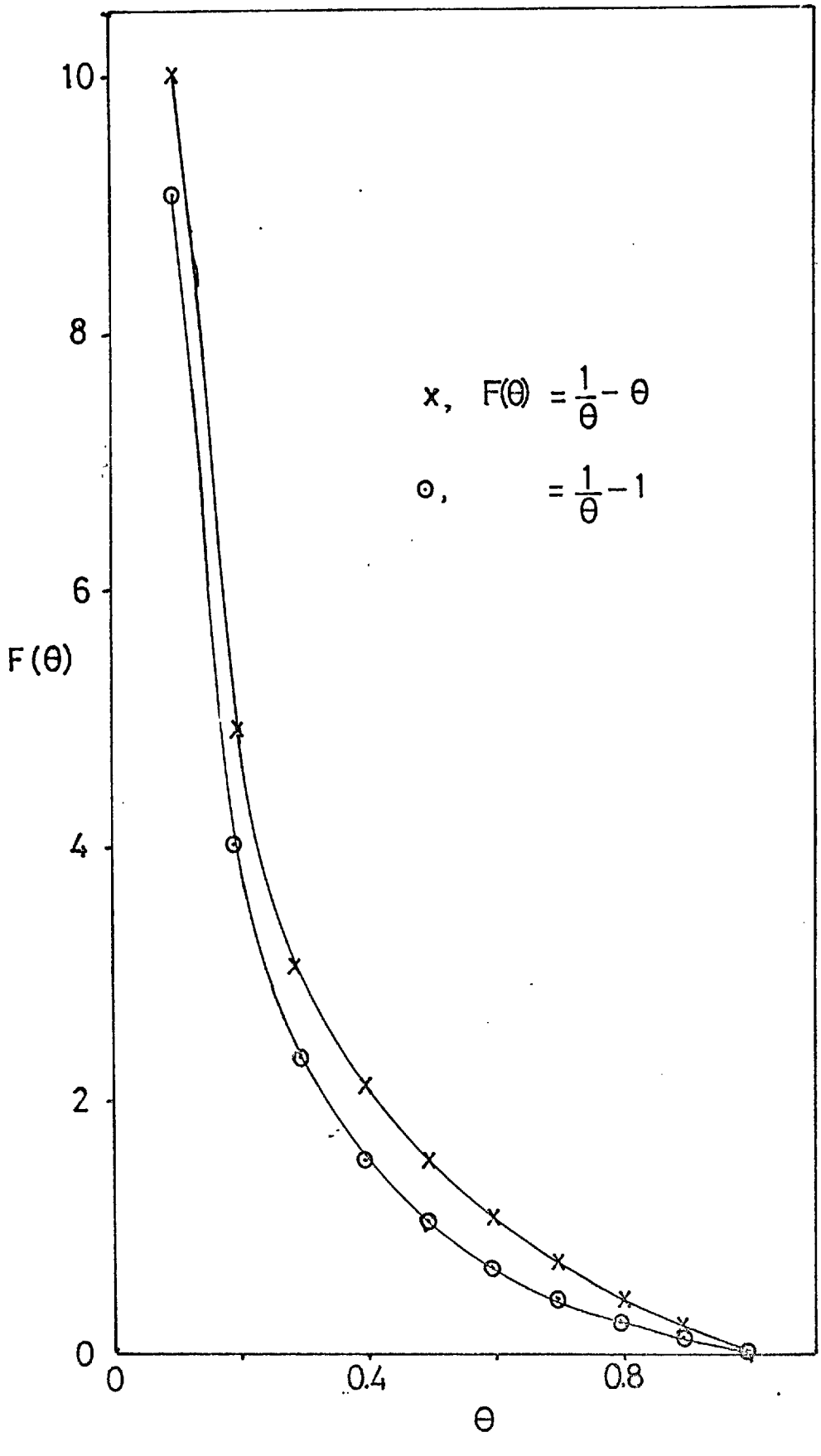
trimethylamine



DE-ACIDITE FF

GRAPH 3.1

COMPARISON OF THE FUNCTIONS $(\frac{1}{\theta} - \theta)$ AND $(\frac{1}{\theta} - 1)$



UPTAKE OF MOLECULAR IODINE BY ION EXCHANGE RESINS

SECTION FOUR

4. UPTAKE OF MOLECULAR IODINE BY ION EXCHANGE RESINS

4.1. INTRODUCTION

The foregoing chapters have identified molecular iodine as the most important and troublesome iodine species in nuclear technology. The majority of the present work was therefore devoted to a study of the mechanism of uptake of elemental iodine. The first part of the work was carried out with Ionac XAX 1284 and 1285 resins, since these were likely to be suitable for the removal of iodine in a wide range of process applications.

Originally work was carried out on the most radiation resistant (73) of the resins, XAX 1285 (15% DVB added). This advantage, however, was offset by the slower rates of reaction caused by the high degree of crosslinking. Consequently, XAX 1284 (10% DVB added) was used for the majority of the later work.

Experiments were also carried out with other ion exchange resins and polystyrene beads in order to elucidate the mechanism of uptake of molecular iodine.

Nitric acid solutions were used most commonly as the solvent for iodine. Although in one case n-heptane was used in order to penetrate polystyrene beads which do not absorb water.

4.2. INVESTIGATION OF THE IODINE SPECIES PRESENT IN NITRIC ACID-IODINE SOLUTIONS

The literature, though somewhat contradictory, suggests that iodine exists mainly in elemental form, although iodates and possible other unidentifiable species can exist at the prevailing nitric acid concentrations in conventional fuel reprocessing cycles. It was therefore thought necessary to confirm the presence of molecular iodine and the

absence of other species in the acidic solutions to be investigated.

In earlier work (142), no iodate was found present in 7.5 mol. $dm.^{-3}$ nitric acid solution. To avoid uncertainty it was decided to check whether other species could be detected using a spectrophotometric technique. (section two).

Scans of potassium iodate, nitric acid, water and I_3^- solution were carried out and are shown in graphs 4.1 - 4.4.

With these standards for comparison a scan of iodine in 7.5 mol. $dm.^{-3}$ HNO_3 solution was performed against a 7.5 mol. $dm.^{-3}$ HNO_3 solution blank. No adsorption due to any of the above was obtained, confirming the original results (142). On this basis, experimental work was initially confined to a study of molecular iodine solutions.

4.3. EXPERIMENTAL DETAILS

Experiments were carried out batchwise. Resin, usually in approximately 0.1 g. quantities, was weighed into 50 $cm.^3$ "Quickfit" glass stoppered flasks. Iodine solution of known concentration was then added to the resin. Solution samples were then taken at suitable time intervals and analysed. The solution concentration was thus obtained directly and the resin concentration could be calculated by difference.

A "blank" was used with all experiments to allow for solution evaporation, and, in the case of radioactive work, the decay of iodine-125. The concentration of the sample was always calculated with respect to the blank.

4.4. EQUILIBRIUM STUDIES

4.4.1. Effect of Crosslinking

The three Ionac XAX resins that were used differed only in the amount of divinyl benzene added to crosslink the structure. Graph 4.5 shows the results of a loading experiment conducted with equal amounts of resin, starting from the same initial iodine concentration, and carried out in the same concentration of nitric acid (7.5 $mol.dm.^{-3}$).

It can be seen that the resin capacity for iodine under these conditions was of a similar order for all the resins, whilst the time taken to approach equilibrium depended on the extent of crosslinking (section 4.5).

This experiment illustrated two points of importance. Since it has already been established that only neutral molecules of iodine are present in a 7.5 $mol.\ dm.^{-3}$ nitric acid solution, the mechanism of uptake cannot be due to an exchange of ions. It would seem, therefore, that iodine was adsorbed into the resin phase.

The second factor that arose from the experiment was the effect of crosslinking on the equilibrium capacity of the resin for iodine. The capacities of the resins under these conditions were similar, in the range 0.27 - 0.31 $mmol.\ g^{-1}$. This difference was not considered to be significant. Later equilibrium work with XAX resins confirmed this conclusion.

4.4.2. Effect of Resin Active Site

It can be seen from table 4.1., that the nature of the active site of the resin plays little part in the uptake of iodine from acid solution. This confirmed that uptake of iodine from acid solution was most likely to be by an adsorptive mechanism.

4.4.3. Effect of Acidity

Graphs 4.10 and 4.6 - 4.9 illustrate the effect of acid concentration on the equilibrium curves for iodine uptake.

It can be seen that there was a vast difference between acid and aqueous solutions. This effect must be due to a change in the resin phase with increasing acidity.

Iodine, being an uncharged species, can only be taken onto the resin by an adsorptive mechanism. Three types of adsorption are possible:-

(i) Physical adsorption: Weak Van der Waals forces between the iodine and the resin matrix.

(ii) Chemisorption:- The actual formation of a bond between the iodine and the resin matrix.

(iii) Adsorption caused by formation of a charge transfer complex: This mechanism is mid-way between the previous two. A partial sharing of the charge, which at one extreme becomes chemisorption and at the other physical adsorption.

The first mechanism could occur on any position in the resin matrix and increasing acidity would probably not have the very marked effect that was observed.

The second mechanism would most likely occur on the aliphatic parts of the resin leading to the formation of iodides. Nitric acid might affect this mechanism but not to the extent observed.

A very large amount of work has been carried out on the charge transfer compounds of iodine (108, 109, 144, 145, 148-155). Iodine forms charge transfer complexes with benzene rings (fig. 4.1) (108, 144, 145, 149, 155). Several possible charge transfer sites are available within the resin matrix, corresponding to the substituted benzene rings (fig. 4.1.). The strength of the complex formed will depend to some extent on the nature of

the groups in or attached to the ring. All the substituents illustrated in fig. 4.1. will lead to a strengthening of the π-electron density of the benzene ring and hence to the strengthening of the charge transfer complex.

The other possible charge transfer site will be on the nitrogen lone pair of the pyridine ring (108, 144, 145, 148-155). The pyridine-iodine interaction has been shown to lead to a very strong charge transfer complex. In fact, there is a considerable evidence for the existence of a variety of pyridine-iodine compounds.

Reid and Mulliken (150) suggest the following reactions:-

$$Py + I_2 \rightleftharpoons Py.I_2 \quad (1)$$

$$Py.I_2 \rightleftharpoons Py.I^+I^- \rightleftharpoons Py.I^+ + I^- \quad (2)$$

$$Py.I_2 + I^- \rightleftharpoons I_3^- + Py \quad (3)$$

$$Py + I_3^- \rightleftharpoons Py.I^+ + 2I^- \quad (4)$$

$$Py + Py.I^+ \rightleftharpoons 2Py^+ + I^- \quad (5)$$

$$Py^+ + Py \rightleftharpoons Py^+Py \quad (6)$$

They suggest that, instead of (2), the following may occur:-

$$Py.I_2 + Py \rightleftharpoons (Py.I)^+(Py.I)^- \quad (7)$$

$$(Py.I)^+(Py.I)^- \rightleftharpoons Py.I^+ + I^- + Py \quad (8)$$

Audrieth and Birr (148) had earlier suggested the following:-

$$Py + I_2 \rightleftharpoons Py.I_2 \quad (9)$$

$$Py.I_2 \rightleftharpoons I.Py^+ + I^- \quad (10)$$

$$I.Py^+ + I^- \rightleftharpoons Py^{++} + 2I^- \quad (11)$$

$$2Py.I_2 \rightleftharpoons I.Py^+ + I.Py.I_2^- \quad (12)$$

Overall the final complexes are likely to be $Py.I_2$ (as $Py.I^+I^-$ or $I.Py^+(I.Py.I_2)^-$) and $Py_2.I_2$ (as $PyI^+.PyI^-$).

The effect of nitric acid on these complexes, especially the latter ones will be considerable. Protonation of the nitrogen in the pyridine ring will have two effects. Firstly, protonation will tend to withdraw electrons from the delocalised π-electrons of the ring. This would weaken any bond formed between these electrons and the iodine molecule. Secondly, and of much greater importance, protonation would block the formation of a nitrogen-iodine charge transfer complex since the nitrogen lone pair would no longer be available.

This latter effect probably explains the results obtained. In aqueous solution the unprotonated nitrogen atoms are able to take up large amounts of iodine. In acid solution the nitrogen is protonated and only the alternative adsorption sites are then available.

One further aspect was apparent from graph 4.10. At higher acid concentrations (above 3 mol. $dm.^{-3}$ nitric acid) the amount of iodine taken on to the resin increased. Although it has been shown (section 4.2) that only molecular iodine was present in7.5 mol. $dm.^{-3}$ nitric acid solution, it is probable that this effect was caused by the formation of iodate within the pores of the resin. Valdesco (156) has shown that there is a higher acid ~~activity~~ concentration within the resin and some iodine oxidation could therefore occur. Exchange between the iodate and the nitrate would therefore lead to increased iodine uptake.

Several points arise from graph 4.6. The capacity of the 10% and 15% crosslinked XAX resins for iodine, was in excess of the capacity as determined by Coady for a univalent species (table 3.1). If the iodine was taken on to the resin as a 1:1 complex (i.e. Py.I_2) it would be expected that the capacity for iodine would have been the same. However, Craske (141) has shown that the theoretical capacity, based on nitrogen

determinations, is approximately 9.0 m.mol. $g.^{-1}$ for an univalent species. Two explanations are therefore possible. Iodine could have utilised more of the nitrogen groups of the resin, or 1:2 complexes with the resin (i.e. $Py_2.I_2$) could be formed. The existence of 1:2 complexes is well documented (eq. (1) to (12)). However, it would be more difficult to form such complexes with a macromolecular structure such as that of the resin. A combination of the two effects probably accounts for the results obtained. The shape of the graph 4.6 was different initially from the other equilibrium curves. This could be due to the formation of uncharacterised species in very dilute aqueous solutions. The existence of these species is well established (section one; 40 - 45).

4.4.4. Polystyrene Bead Experiments

The effect of the outer surface of a resin was studied by using polystyrene beads. Such beads do not swell in aqueous solution and water will not diffuse into the interior matrix.

Iodine uptake from aqueous solution was found to be strongly dependent on the degree of crosslinking of the bead (graph 4.11), contrasting with the resin results. On such a bead the most likely adsorption site is on benzene rings of the outer surface (fig. 4.1). Consequently the conclusion drawn was that increasing crosslinking increased the number of benzene rings on the outer surface of the bead. The molecular explanation could be that inhomogeneities in the crosslinking (146, 147) lead to a higher concentration of benzene rings on the surface at higher crosslinking.

The adsorption of iodine per gram of bead was also shown to be strongly dependent on the mesh size of the bead (graph 4.12). Since a smaller bead has a larger surface area per gram these results confirm the surface as the adsorption site for iodine.

Finally, the effect of solvent on the adsorption was studied. It was thought that a solvent which diffused into the bead would cause enhanced adsorption. This was not the case (graph 4.13). n-Heptane had been chosen as the solvent because of its neutrality to iodine. Two factors of importance were illustrated by this experiment. Firstly, in an adsorption study the importance of solvation should not be forgotten. Secondly, solvent adsorption can also be important. On a non-polar, molecular matrix, such as polystyrene, non-polar hydrocarbons such as n-heptane will be adsorbed (72). There could be sufficient solvent adsorption to block the uptake of molecular iodine.

4.4.5. Interpretation of Equilibrium Results

The only isotherm that has been successfully applied to the adsorption of iodine onto a wide range of adsorbents is the Freundlich isotherm:-

$$\frac{\bar{x}}{\bar{m}} = \alpha C^{1/n}$$

or in logarithmic terms,

$$\log \frac{\bar{x}}{\bar{m}} = \frac{1}{n} \log C + \log \alpha$$

A log-log plot of resin phase concentration versus solvent phase concentration should yield a straight line of slope 1/n. The value of α may then be calculated by substitution.

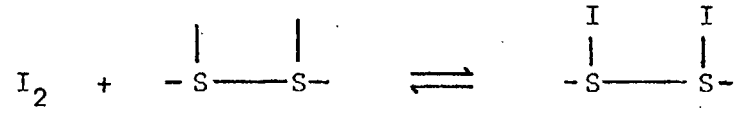
Some of the equilibrium data obtained for the XAX resins was plotted in this way (graphs 4.14-4.16). All of the curves approximated to straight lines over a limited range. Indeed, in the case of adsorption from aqueous solution there appeared to be two straight lines corresponding to the two curve structure shown in graph 4.6. This treatment has been shown to

correspond to an exponential distribution of adsorption sites (171), and there was no evidence to suggest that this should be the case with the resin.

An attempt was also made to see if the data fitted a Langmuir isotherm. Two reactions can possibly describe the adsorption of iodine:-

(13)

where S represents the adsorption site within the resin matrix,



(14)

Reaction (13) corresponds to the simple Langmuir equation (eq. 11 section 3.3.1.),

$$\frac{x}{x_m} = \frac{kc}{1 + kc} \qquad (15)$$

which in terms of the fraction of sites occupied θ, may be written,

$$kc = \frac{\theta}{1 - \theta} \qquad (16)$$

where k is a constant.

For the case of adsorption with dissociation, eq. (14), the Langmuir form may be written (170),

$$kc = \left(\frac{\theta}{1 - \theta}\right)^2 \qquad (17)$$

Graphs 4.17 and 4.18 illustrate that these two approaches are unsatisfactory for the system studied. These isotherms apply only to the "ideal"

case of physical adsorption, although approximate fits can often be obtained. It is therefore unlikely that iodine adsorption onto an ion exchange resin is a purely physical process.

One final adsorption isotherm, proposed by Slygin and Fumkin (172):-

$$\theta = \frac{1}{f} \ln a c \qquad (18)$$

where f, a are empirical constants, was found to fit the data reasonably well. (graph 4.19). This isotherm has been interpreted theoretically (173) on the assumption that the heat of adsorption is a function of the fraction of surface covered. It is possible that this may be the valid in this case.

None of these interpretations are totally satisfactory for iodine adsorption. This is particularly so in the case of adsorption from aqueous solution. With all aqueous isotherms a two curve structure was obtained. Possible ~~The~~ reasons for this have already been discussed (section 4.4.3.).

These results indicated that neither pure chemisorption nor pure physical adsorption was occurring

4.5. KINETIC STUDIES

A detailed investigation of the rate of approach to equilibrium was carried out, in order to discover the kinetic parameters of importance.

4.5.1. Effect of Crosslinking

Graph 4.5 illustrates the effect of crosslinking on the attainment of equilibrium. The initial iodine solution concentration and the weight of resin used was the same in each case. The final capacity of the three resins was also similar. However, the highly crosslinked (15% D.V.B.) resin took much longer to attain equilibrium. Throughout the work this was always the case. This indicates that increased crosslinking hinders the approach to equilibrium and is symptomatic of a resin-phase diffusion

controlled mechanism.

4.5.2. Interpretation of Kinetic Results

The first kinetic data to be analysed ~~was~~ were based on the uptake of iodine from 7.5 mol. dm^{-3} nitric acid solution onto XAX 1285. Graph 4.20 shows the resin concentration as a function of time. Different original iodine solution concentrations were used with approximately equal amounts of resin.

In order to analyse these data, plots were firstly made of the solution concentration with respect to time. The slopes of these curves were then measured at different times (e.g. graph 4.21), since

$$V = \frac{d[I_2]}{dt}\ \text{resin} = -\frac{d[I_2]}{dt}\ \text{solution},$$

either rate of change could have been chosen. From these data, plots of the rate of change of iodine concentration versus time could be made (graph 4.22).

The methods initially used for kinetic analysis were those suggested by Frost and Pearson (159) and Laidler (160). The rate of reaction may be related to the concentration of the reactant by:-

$$V = kc^n \qquad (1)$$

where k is a constant and n the order of reaction. Then,

$$\log V = \log k + n \log c \qquad (2)$$

and the slope of the log-log plot of rate versus concentration gives the order of reaction. From the experiments performed (graph 4.22), the original rates could be found. Hence, from this, the true order of the

reaction without the influence of intermediates could be calculated (graph 4.23).

The rate was determined as an average taken over the first day, as the initial rate was difficult to determine (see later). This gave the approximate order, which was first order. This indicated that initially the rate was dependent directly on the iodine concentration, i.e. the following reaction was occurring:-

$$[I_2]_{solution} \rightleftharpoons [I_2]_{resin}$$

However, when the log-log graph for a single experiment is plotted, the rate order with respect to time can be obtained (graph 4.24). This was found to be 2.4, indicating that the rate decreased with time. This could be due to the formation of some intermediate, the variation of energy of adsorption sites or, more likely, a diffusion effect in the resin phase.

This method of analysis was not completely valid. Graph 4.22 illustrates the variation of rate of "reaction" with time. All the graphs appear to be asymptopic to both ordinate and abscissa. Therefore, it cannot be positively said that the initial rate was first order. However, the rate order did increase with time and the above explanation for this is probably correct.

Mathematical functions have been proposed for the analysis of kinetic data (section 3.3.2):-

$$\frac{d\theta}{dt} = K\left(\frac{1}{\theta} - 1\right) \qquad (3)$$

$$\frac{d\theta}{dt} = -K\left(\theta - \frac{1}{\theta}\right) \qquad (4)$$

$$\frac{d\theta}{dt} = K(1 - \theta) \qquad (5)$$

These three functions were plotted for the iodine data of graph 4.22 (graphs 4.25 - 4.27). Equation (5) (graph 4.28) was found to be inapplicable to the iodine adsorption. Equations (3) and (4) (graphs 4.25, 4.26) approximate to straight lines, equation (3) being the better of the two. Also equation (4) has generally been applied to ion exchange problems and can be interpretated as a simplification of the general rate law of ion exchange (129, 130).

Equation (3) can be considered to correspond to a situation where energy was available to cause a transition to a resin associated state. The rate controlling step could then be diffusion in the resin phase. The initial rapid rate would be because some adsorption sites were readily attainable by iodine, e.g. on the surface of the resin. The rate would then decrease faster than the total number of unoccupied sorption sites because further sites would be difficult to attain.

Overall, as the fraction of sites occupied increased the rate decreased. This indicated that the greater the coverage of the resin the more difficult it was to occupy further sites. This picture ties in well with the Slygin and Fumkin equilibrium isotherm, that best fitted the adsorption (section 4.4.4.).

The further validity and use of equation (3) was shown by graphs 4.28 - 4.30. These lines were drawn from experiments with a variety of conditions. Instead of using the dimensionless parameter θ, the actual resin concentration, $\bar{c}$, was used. Since,

$$\frac{\bar{c}}{\bar{c}_\infty} = \theta \qquad (6)$$

and $\bar{c}_\infty$ = equilibrium resin concentration, which is a constant for each experiment equation (3) was still valid, rewritten as,

$$-\frac{dc}{dt} = k_2\left(\frac{1}{\bar{c}}\right) - k_1 \qquad (7)$$

where c = solution concentration

k_1, k_2 = constants.

then when $\frac{dc}{dt} = 0$, $\bar{c} = \bar{c}_\infty$ and,

$$\bar{c} = \frac{k_2}{k_1} = \bar{c}_\infty \qquad (8)$$

This constant ~~k_2/k_1~~ k_1/k_2 will be the intercept on the abscissa of the graph of $-\frac{dc}{dt}$ versus $(\bar{c})^{-1}$. Hence, for a linear relationship such as eq. (7); a few readings taken early in an experiment enable the equilibrium capacity of the resin to be determined.

4.6. ELUTION STUDIES

Elution of a few samples was attempted in order to get further information on the mechanism of iodine uptake.

Firstly, a resin sample equilibrated from aqueous solution was acidified to 0.6 mol. $dm.^{-3}$ nitric acid concentration by the addition of one $cm.^3$ of concentrated nitric acid (15.7 mol $cm.^{-3}$). (Graph 4.3).

This graph confirmed previous conclusions in two ways:-

(i) Initial immediate rise in iodine solution concentration was due to the breaking of the iodine-pyridine charge transfer complex,

$$\text{Resin} - \text{Py}^{\delta+}\text{---}{}^{\delta-}\text{I}\text{——}\text{I} \quad + \quad \text{H}^+\text{NO}_3^- \rightleftharpoons \text{Resin} - \text{Py:H}^+\text{NO}_3^- + \text{I}_2$$

confirming the presence of the complex.

(ii) The reaction was resin phase diffusion controlled. It took a very short time for the acid to diffuse to the resin and for some iodine to diffuse back into solution. The reaction rate then falls off rapidly as the acid and iodine have to diffuse respectively further into and out of the resin.

A further series of samples equilibrated from aqueous solutions were adjusted to 1 mol. $dm.^{-3}$ nitric acid in solution and allowed to equilibrate. These results were plotted on graph 4.7. It can be seen that the results lie on the graph. This indicated that the loading was at the least very close to being totally reversible.

4.7. SUMMARY OF MOLECULAR IODINE LOADING EXPERIMENTS

(1) The only detectable species present in the 7.5 mol. $dm.^{-3}$ nitric acid-iodine system was molecular iodine.

(2) Crosslinking of the XAX resins had only a slight effect on the equilibrium capacity of the resin for iodine. However, the rate of uptake of iodine increased with decreasing crosslinking.

(3) The iodine uptake depended on the surface area in contact with the solution, uptake increased with smaller beads, i.e. larger surface area, for polystyrene beads.

(4) The iodine solvent plays a part in the amount of iodine uptake onto polystyrene beads.

(5) The active exchange site of the resin had little effect on adsorption from acidic solution.

(6) Acidity of solution had a great effect on iodine uptake onto XAX resins. In aqueous solution iodine formed a charge transfer complex with the pyridine of the resin leading to a high capacity. The capacity decreased to a minimum around 2 mol. $dm.^{-3}$ nitric acid concentration, and then rose

again possibly due to formation of other iodine species, within the resin phase.

(7) The Slygin and Fumkin isotherm was a reasonable fit of the iodine adsorption onto the XAX resins.

(8) The equation $\frac{d\theta}{dt} = k(\frac{1}{\theta} - 1)$ could be used to predict the ultimate iodine capacity of the resin.

(9) Diffusion in the resin phase was the rate controlling step in the uptake of iodine onto the resins.

(10) The adsorption of iodine onto the resin in aqueous solution was largely reversible.

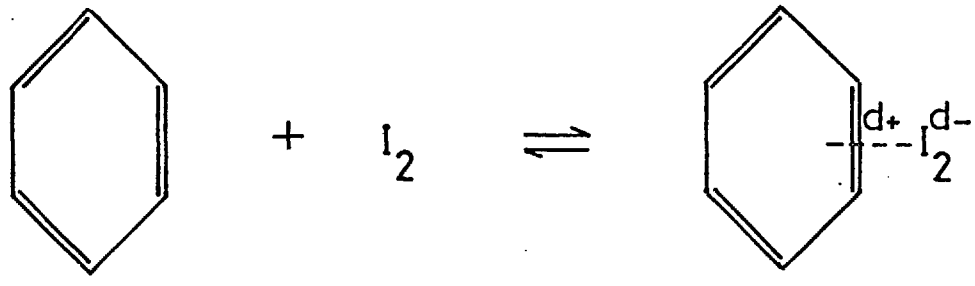
TABLE 4.1.

COMPARISON OF IODINE LOADINGS (m mol.g.$^{-1}$) FROM 7.5 mol.dm.$^{-3}$ NITRIC ACID SOLUTION USING VARIOUS ION EXCHANGE RESINS, SAME INITIAL IODINE CONCENTRATION, EQUAL MASSES OF RESIN

RESIN	% DVB ADDED	IODINE LOADING m mol.g.$^{-1}$
Zeocarb 225	8	0.273
Deacidite FF	8	0.163
IONAC XAX	5	0.280
	10	0.313
	15	0.270

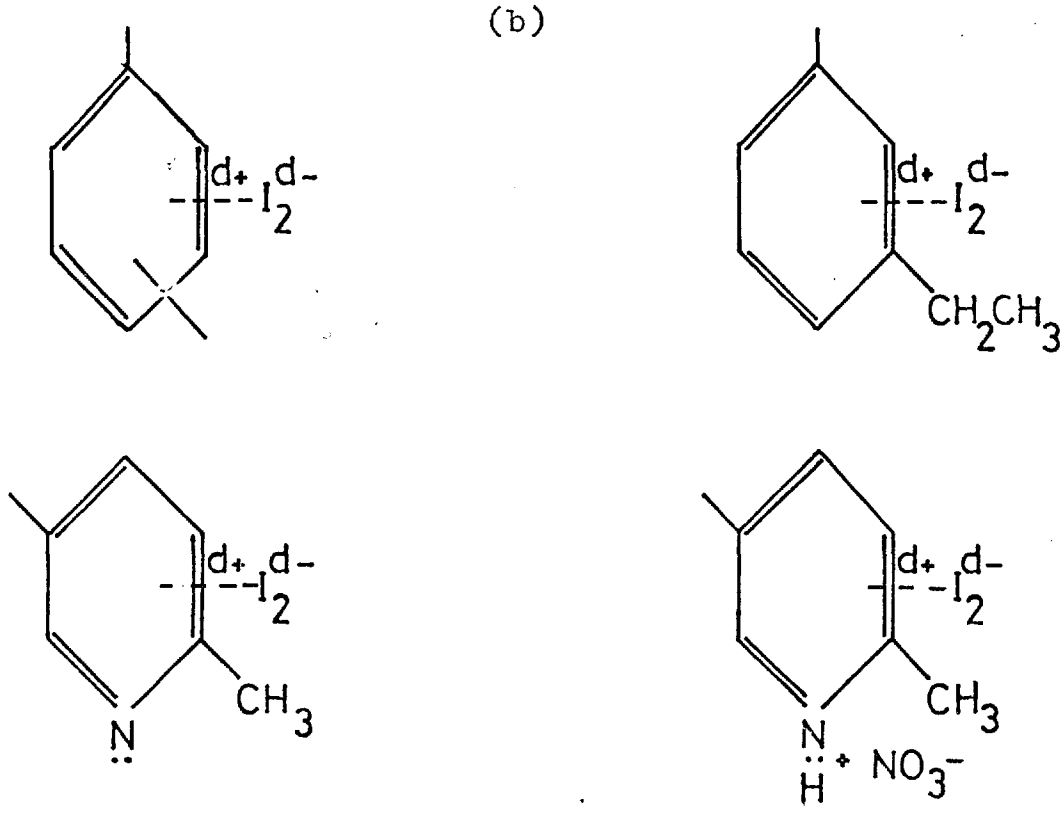
FIGURE 4.1

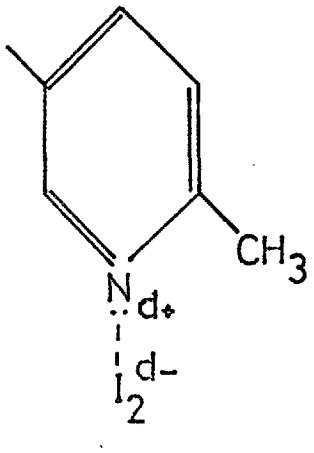
(a)



Charge transfer mechanism

(b)

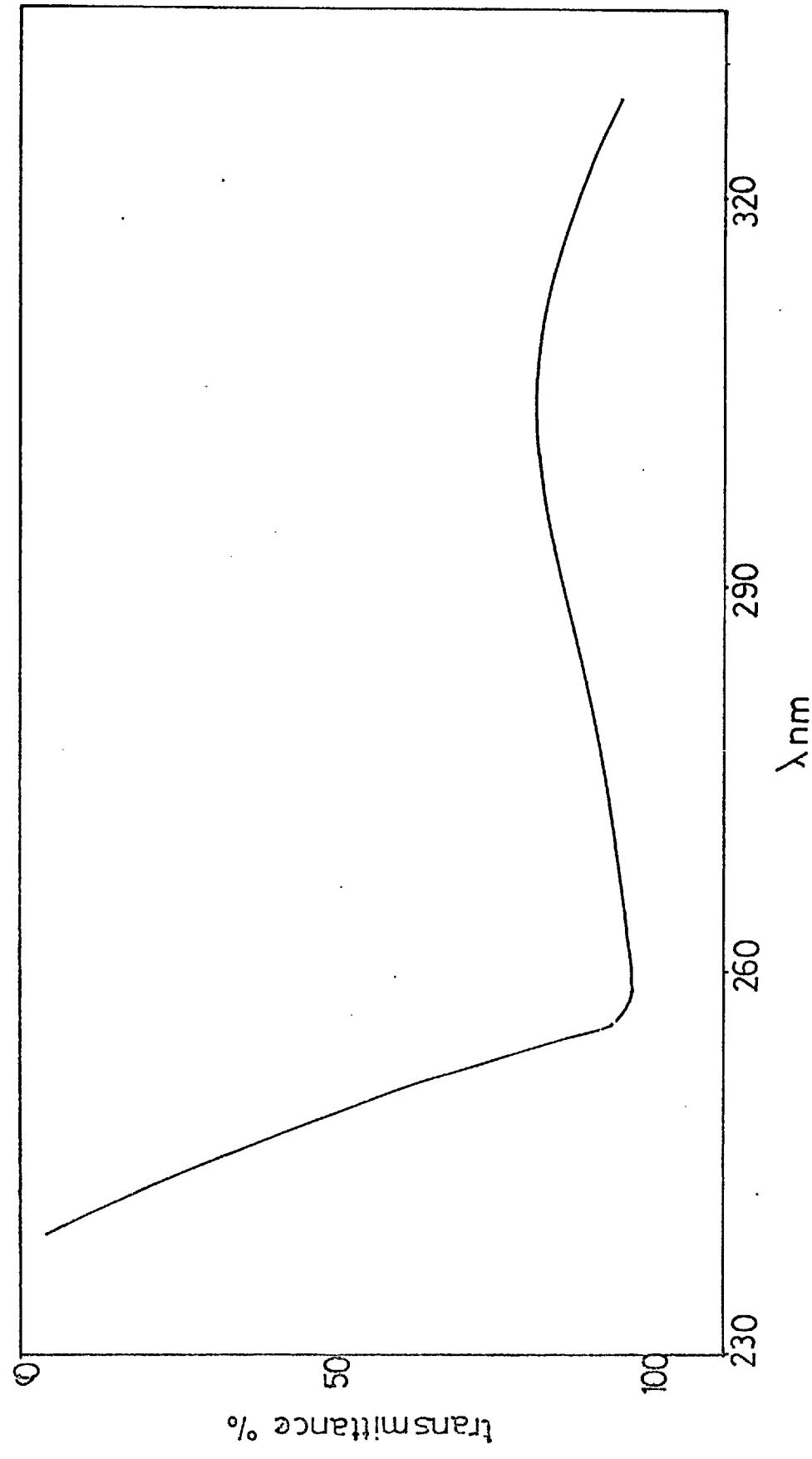




Possible adsorption sites on polystyrene beads and Ionac XAX resins

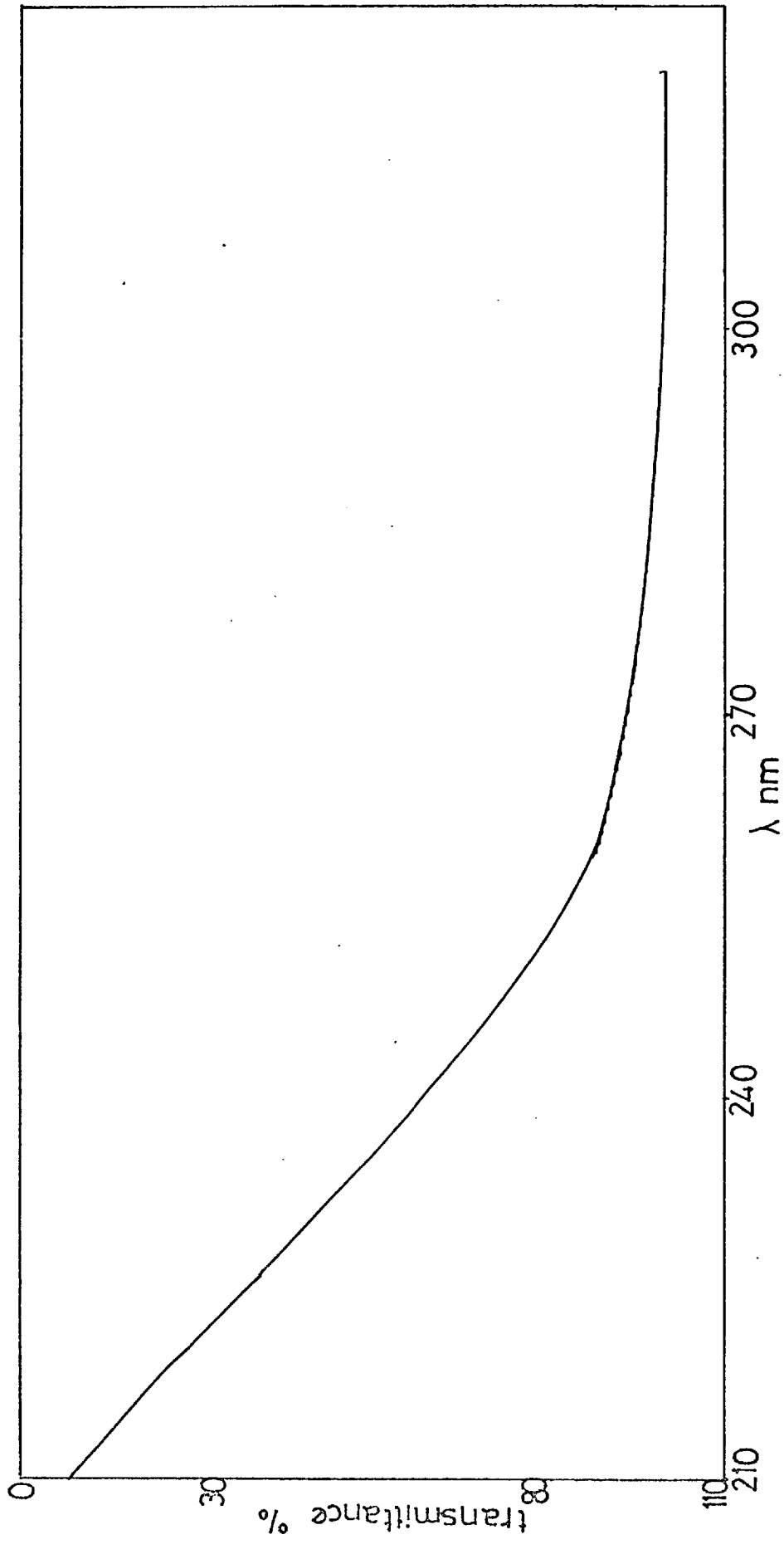
GRAPH 4.1

TRANSMITTANCE (%) OF NITRIC ACID SOLUTION IN THE WAVELENGTH RANGE 240-330 nm.



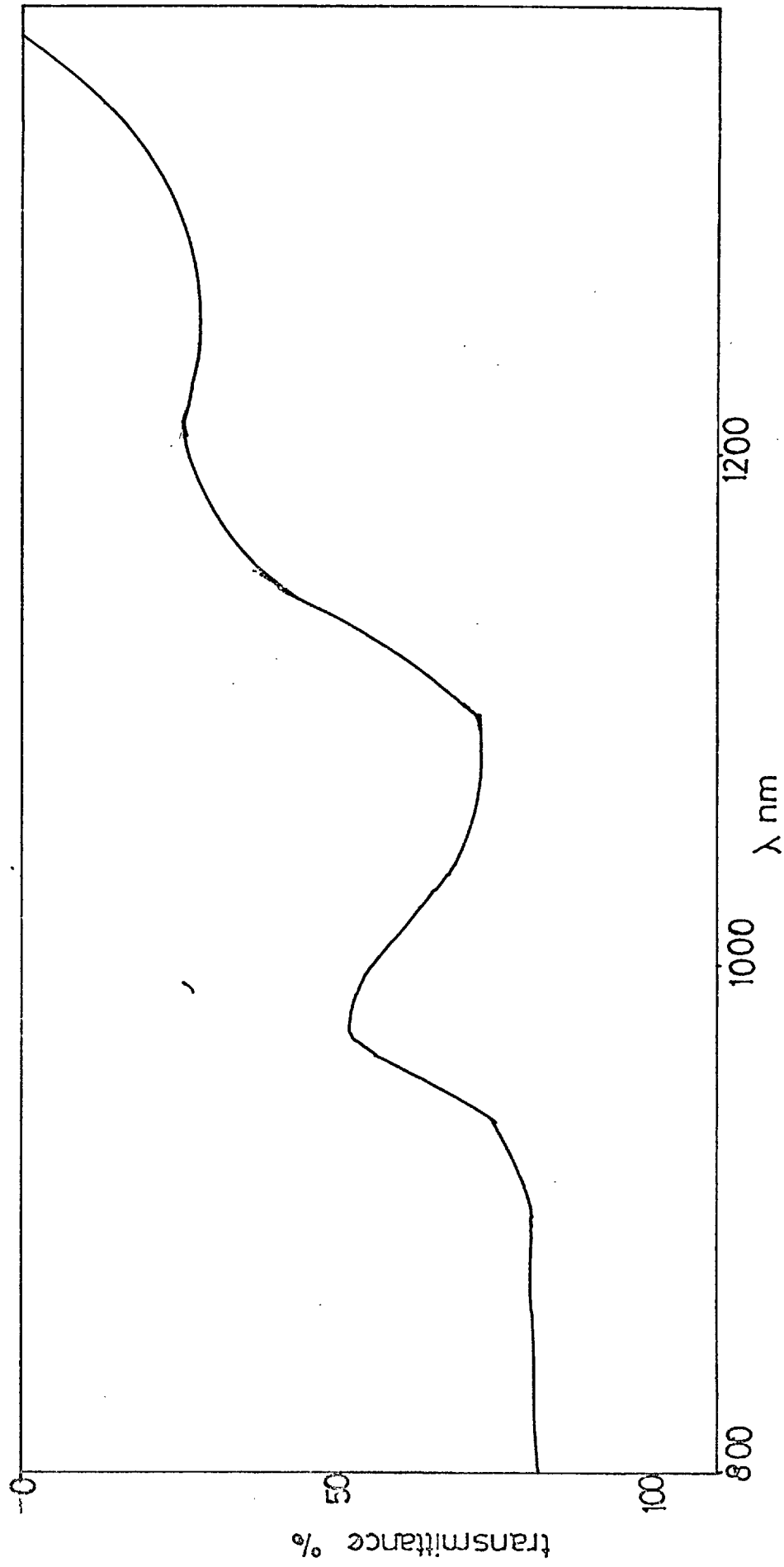
GRAPH 4.2

TRANSMITTANCE (%) OF POTASSIUM IODATE SOLUTION IN THE WAVELENGTH RANGE 210-320 nm.



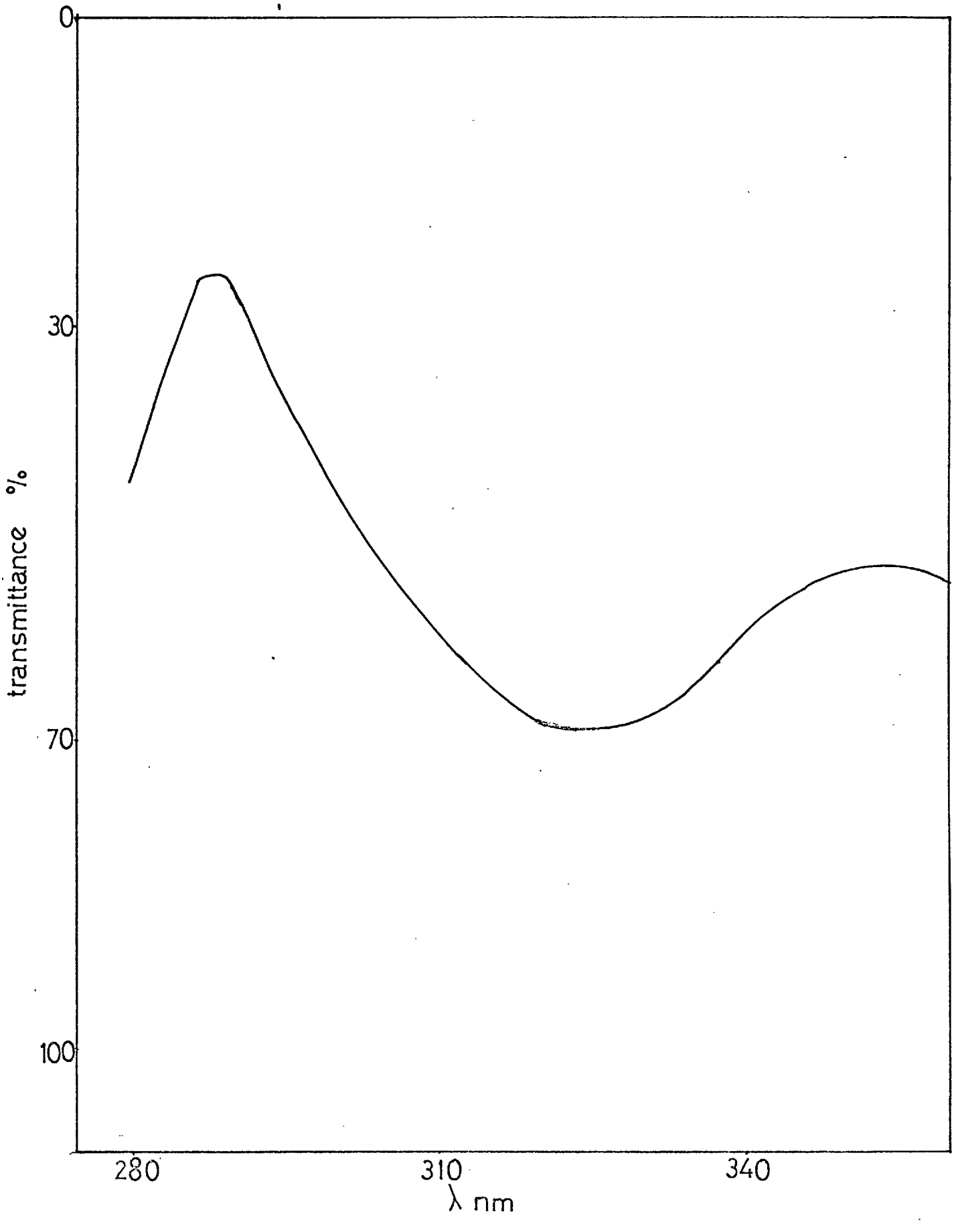
GRAPH 4.3

TRANSMITTANCE (%) OF WATER IN THE WAVELENGTH RANGE 800 - 1350 n.m.



GRAPH 4.4

TRANSMITTANCE (%) OF I_3^- IN THE WAVELENGTH RANGE 280 - 360 nm.

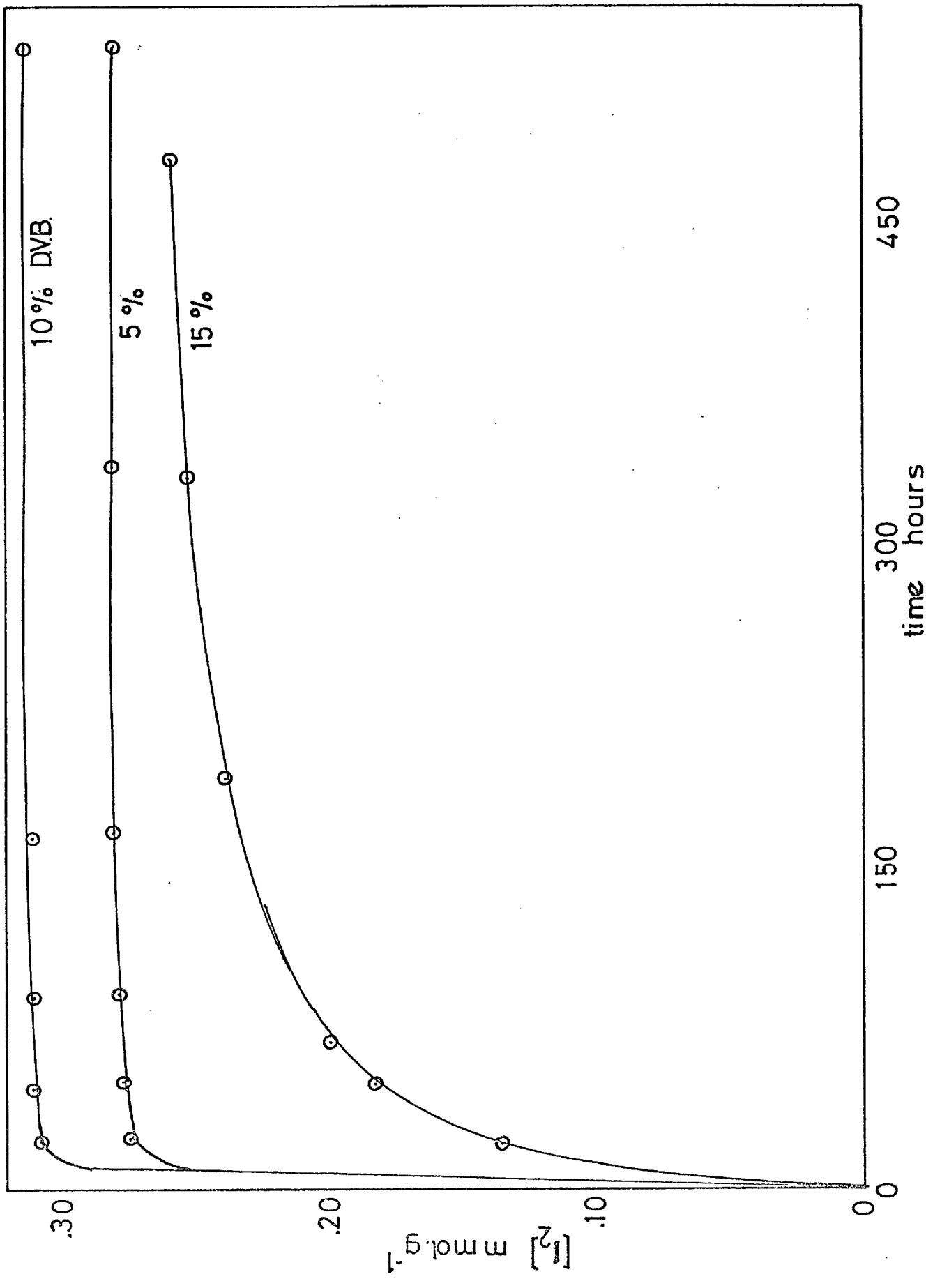


GRAPH 4.5

RESIN CONCENTRATION (m.mol. g^{-1}) AGAINST TIME (hours)

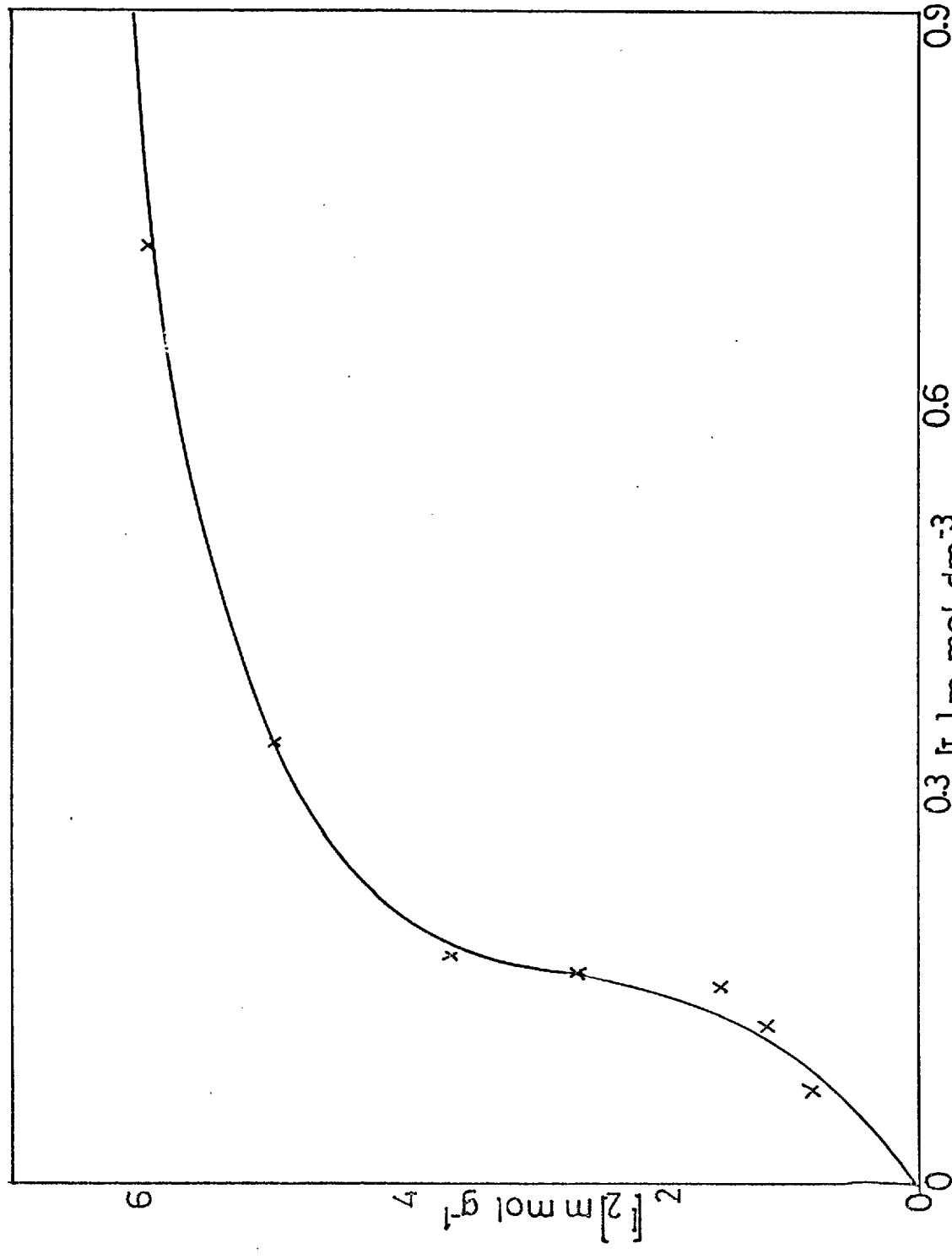
SHOWING EFFECT OF CROSSLINKING

XAX RESINS, 7.5 mol.dm^{-3} HNO_3



GRAPH 4.6

EQUILIBRIUM CONCENTRATIONS OF IODINE IN AQUEOUS SOLUTION ($m.mol.\ dm^{-3}$) WITH THE RESIN XAX 1284 ($m.mol.\ g^{-1}$)

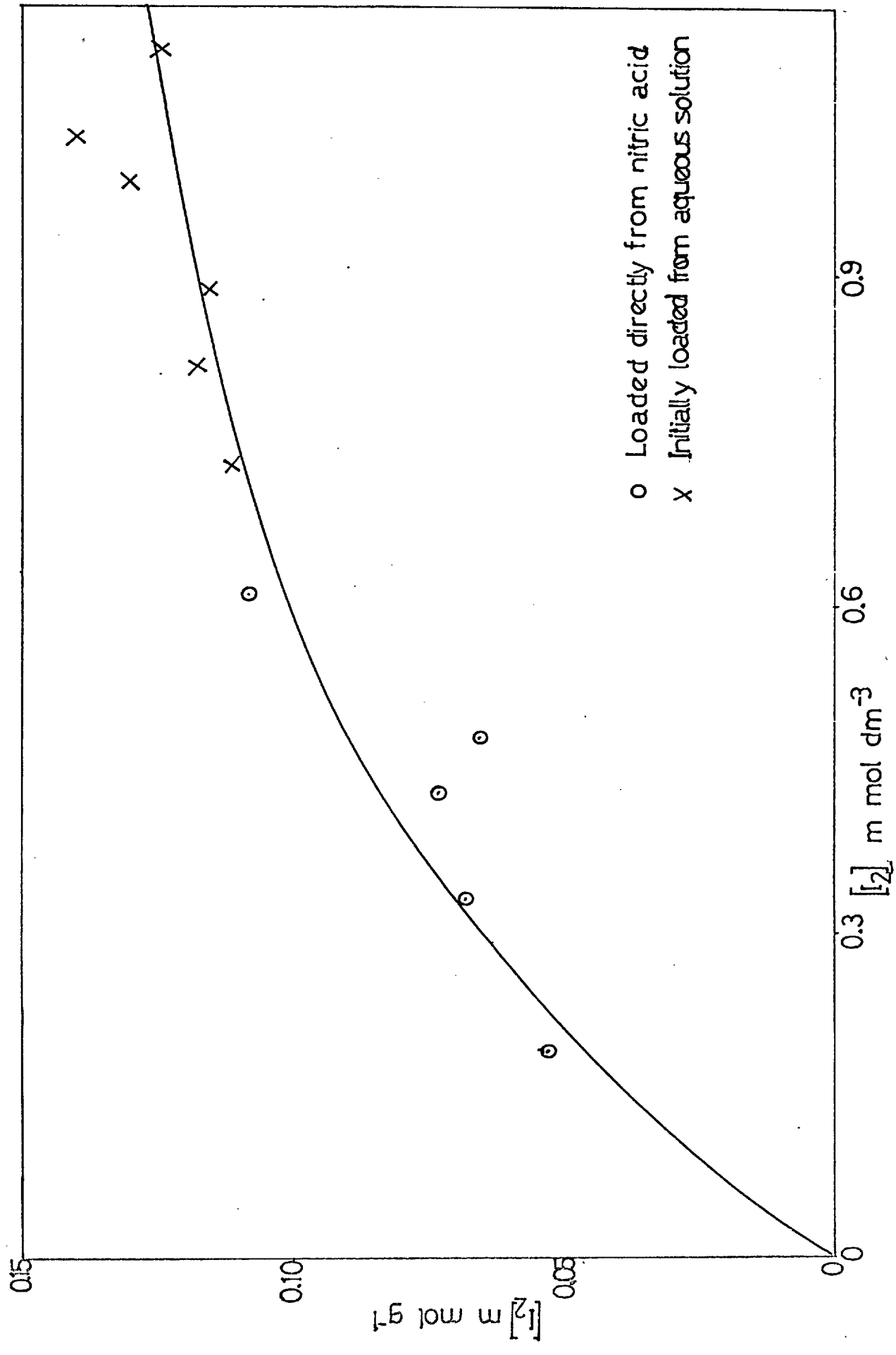


GRAPH 4.7

EQUILIBRIUM CONCENTRATIONS OF IODINE (m.mol. dm^{-3})

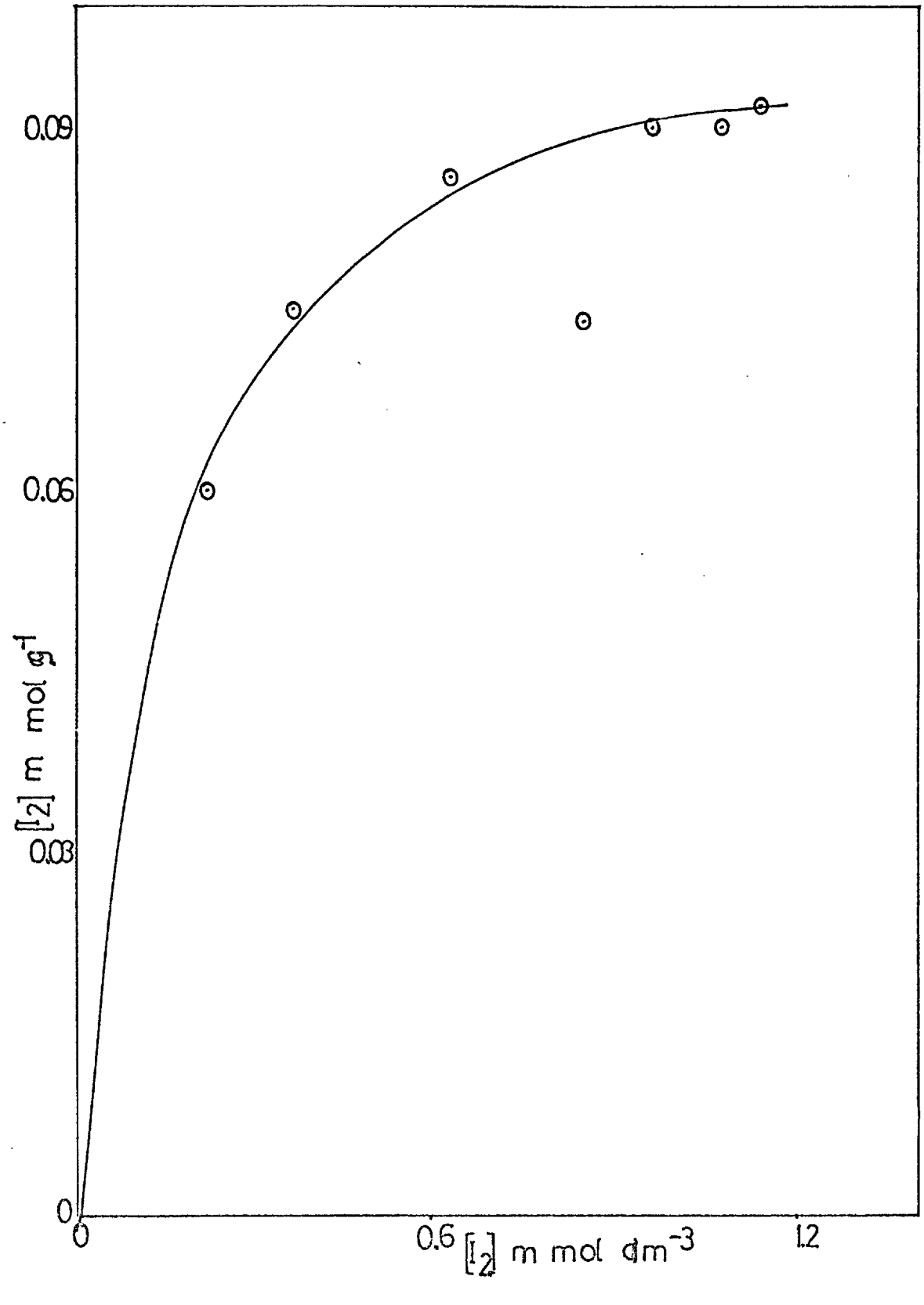
IN 1mol. dm^{-3} NITRIC ACID SOLUTION (m.mol. dm^{-3})

WITH THE RESIN XAX 1284 (m.mol. g^{-1})



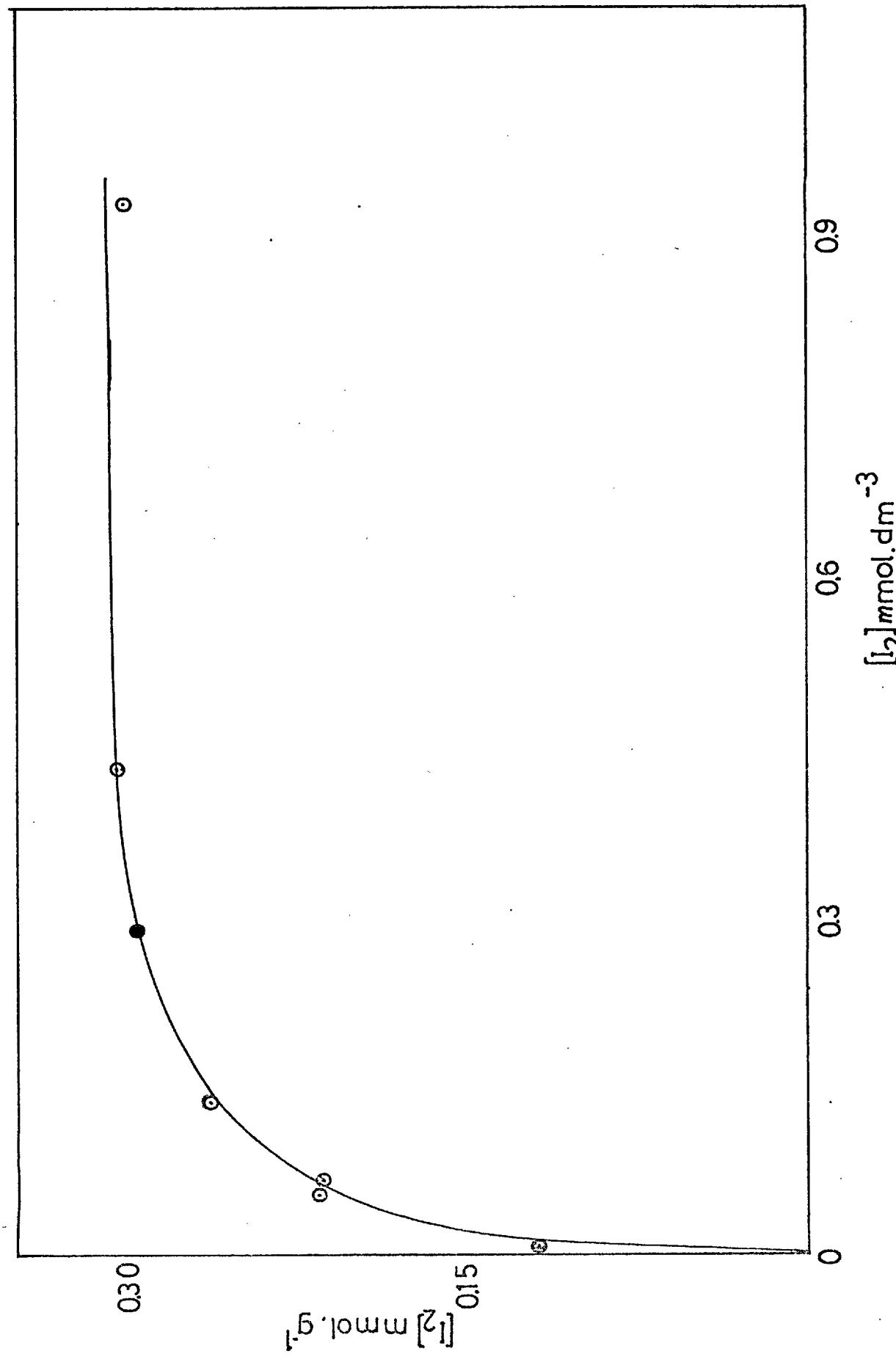
GRAPH 4.8

EQUILIBRIUM CONCENTRATIONS OF IODINE (m.mol. dm^{-3}) IN 3.75 mol. dm^{-3} NITRIC ACID SOLUTION WITH THE RESIN XAX 1284 (m.mol. g^{-1})



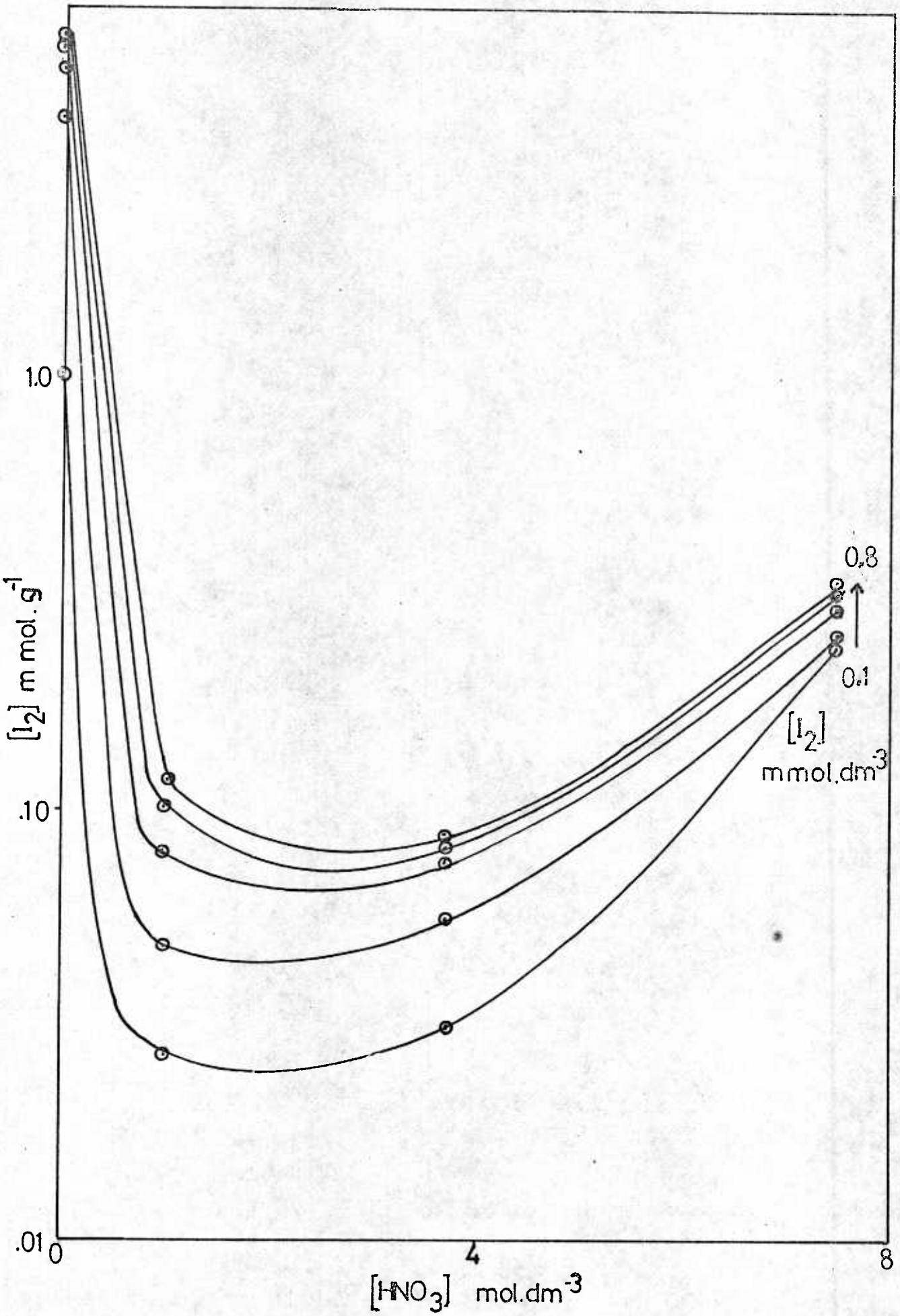
GRAPH 4.9

EQUILIBRIUM CONCENTRATION OF IODINE (m.mol. dm^{-3}) IN 7.5 mol. dm^{-3} NITRIC ACID SOLUTION WITH THE RESINS XAX 1284, 1285 ($\bar{m}$. mol. g^{-1})



GRAPH 4.10

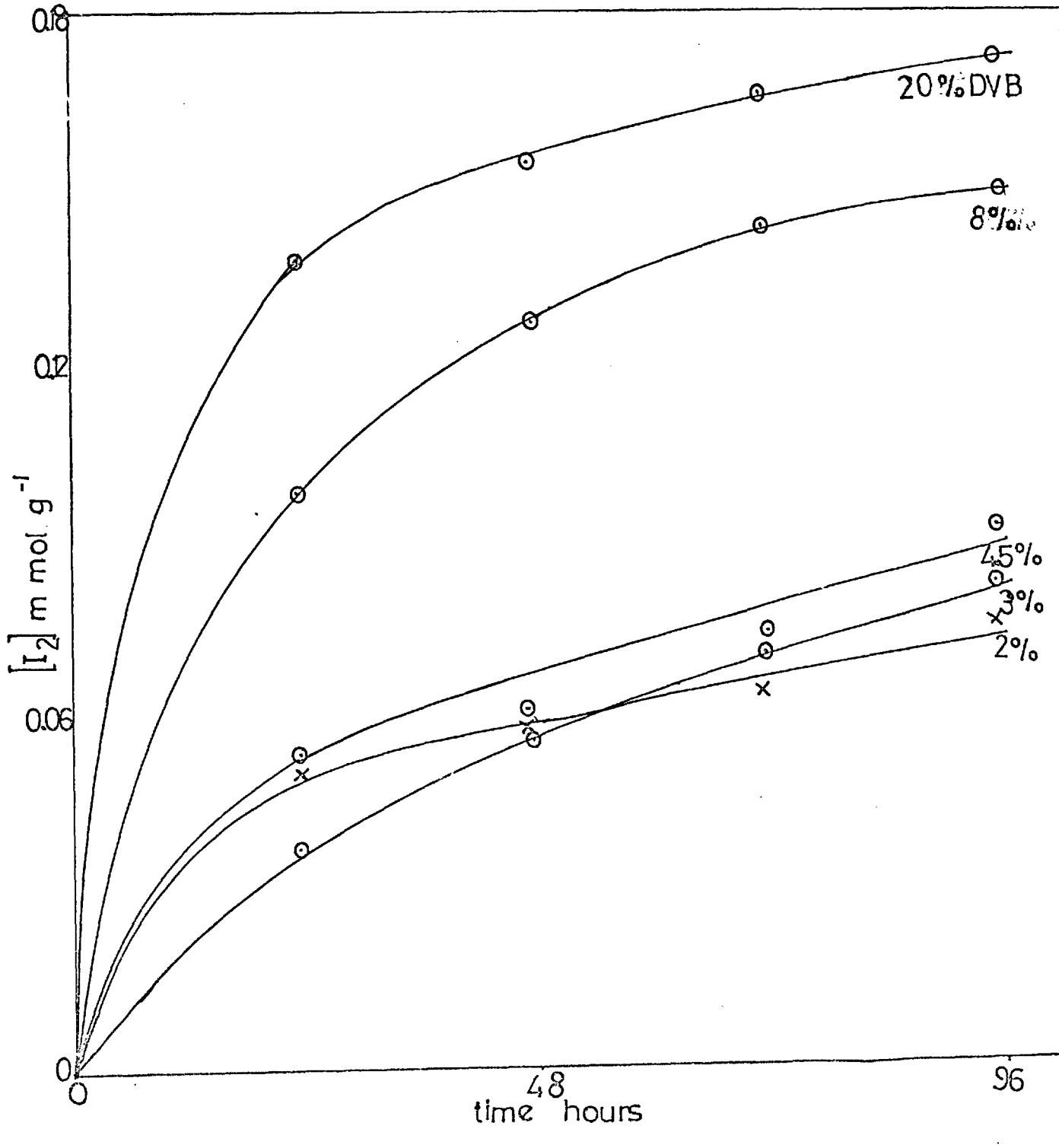
RESIN CONCENTRATION OF IODINE (m.mol. g^{-1}) VERSUS NITRIC ACID CONCENTRATION (m.mol. dm^{-3}) AT DIFFERENT IODINE SOLUTION CONCENTRATIONS (m.mol. dm^{-3})



GRAPH 4.11

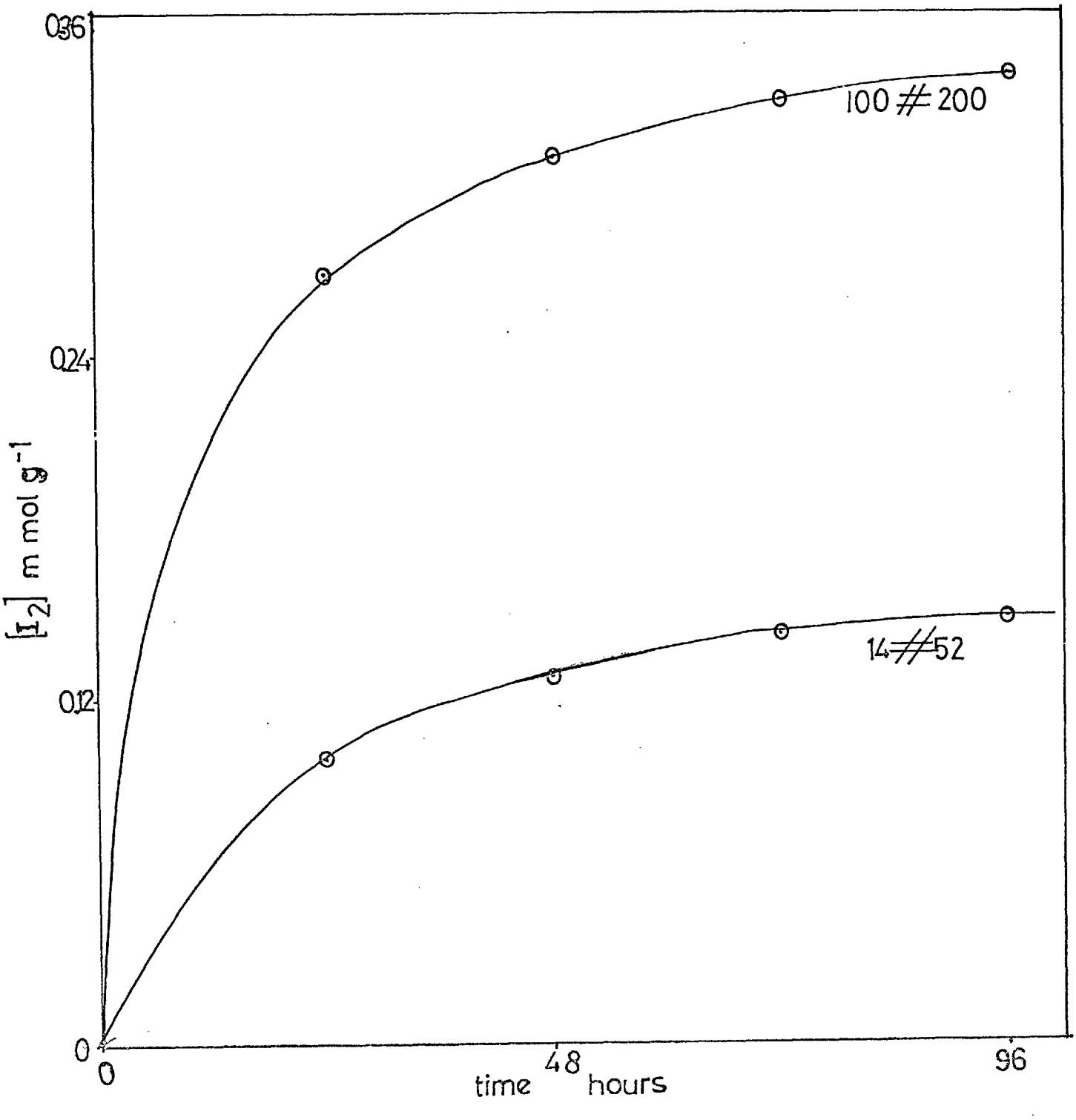
CAPACITY OF POLYSTYRENE BEADS (m.mol. g^{-1}) VERSUS TIME (hours) SHOWING THE EFFECT OF CROSSLINKAGES

AQUEOUS SOLUTION



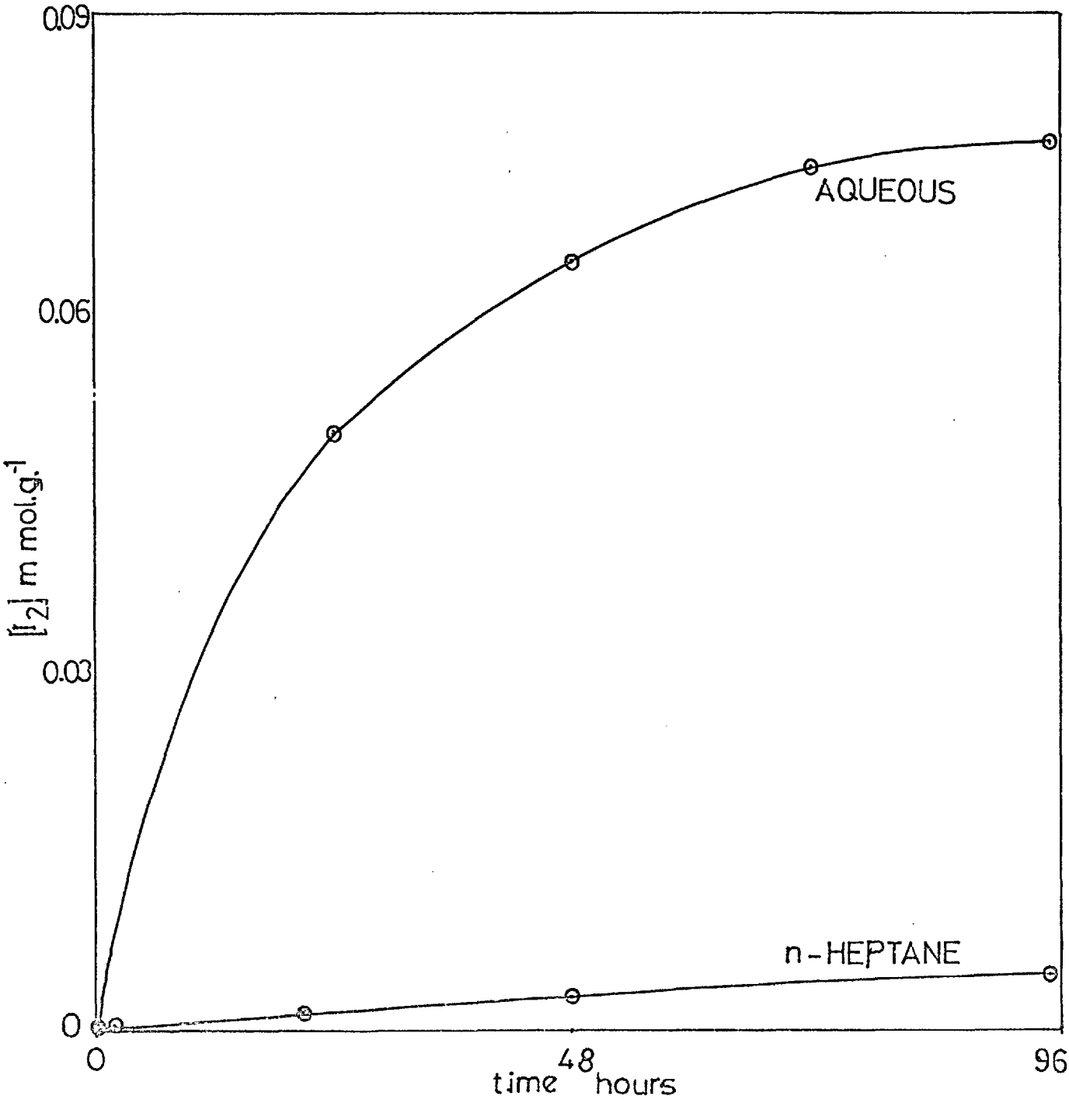
GRAPH 4.12

CAPACITY OF POLYSTYRENE BEADS (m.mol. g^{-1}) VERSUS TIME (hours) SHOWING THE EFFECT OF BEAD SIZE. AQUEOUS SOLUTION, 8% D.V.B.



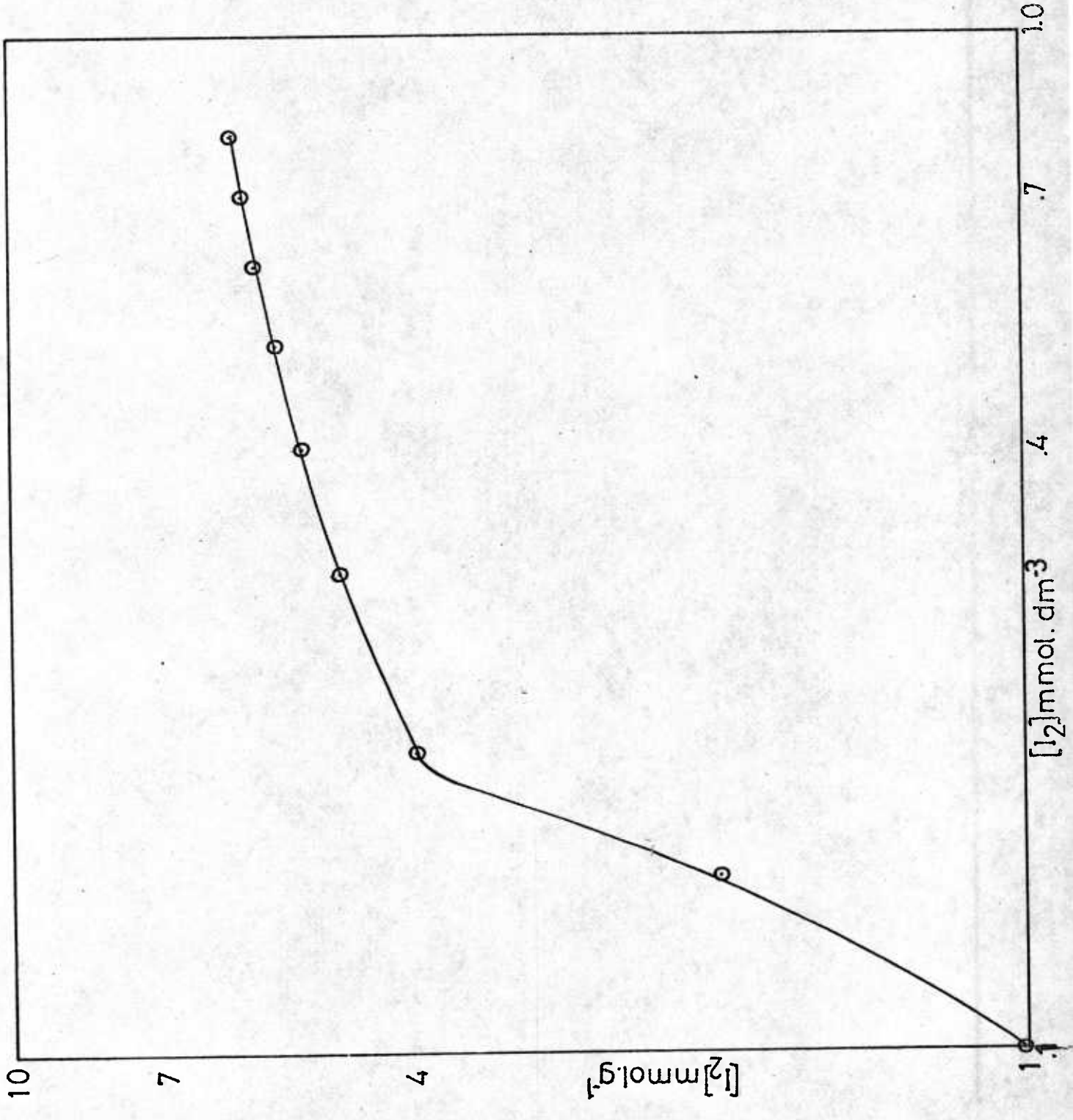
GRAPH 4.13

COMPARISON OF IODINE UPTAKE (m.mol. g^{-1}) ON TO POLYSTYRENE BEADS (8% D.V.B.) FROM AQUEOUS AND n-HEPTANE SOLUTIONS WITH RESPECT TO TIME (hours)



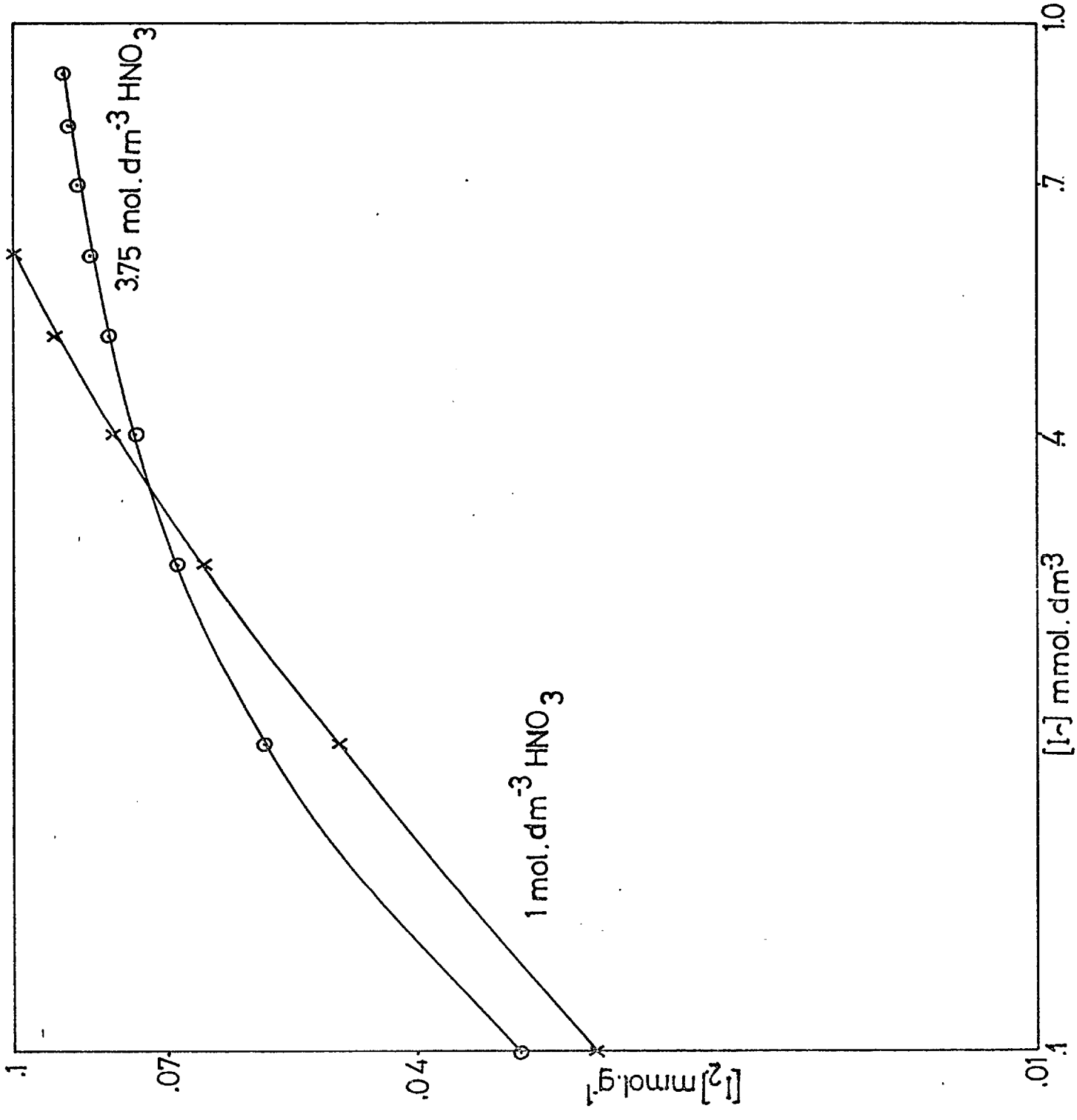
GRAPH 4.14

FREUNDLICH ISOTHERM PLOT OF EQUILIBRIUM CONCENTRATIONS OF IODINE IN SOLUTION (m.mol. dm^{-3}) AND ON THE RESIN (m.mol. g^{-1}) IN AQUEOUS SOLUTION



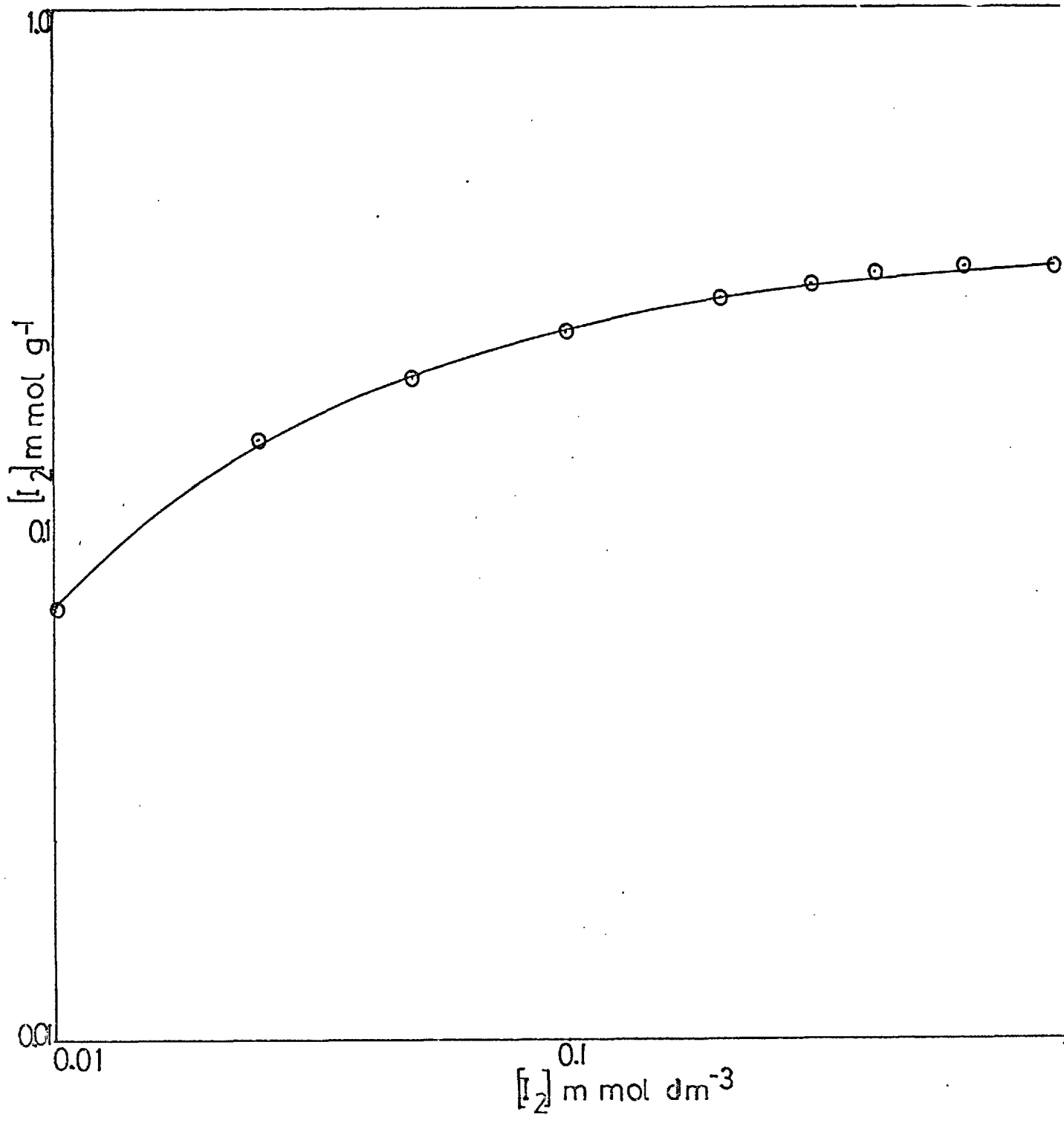
GRAPH 4.15

FREUNDLICH ISOTHERM PLOT OF EQUILIBRIUM CONCENTRATIONS OF IODINE IN SOLUTION (n.mol. dm^{-3}) AND ON THE RESIN (n.mol. g^{-1}) IN 1 AND 3.75 mol. dm^{-3} NITRIC ACID SOLUTIONS



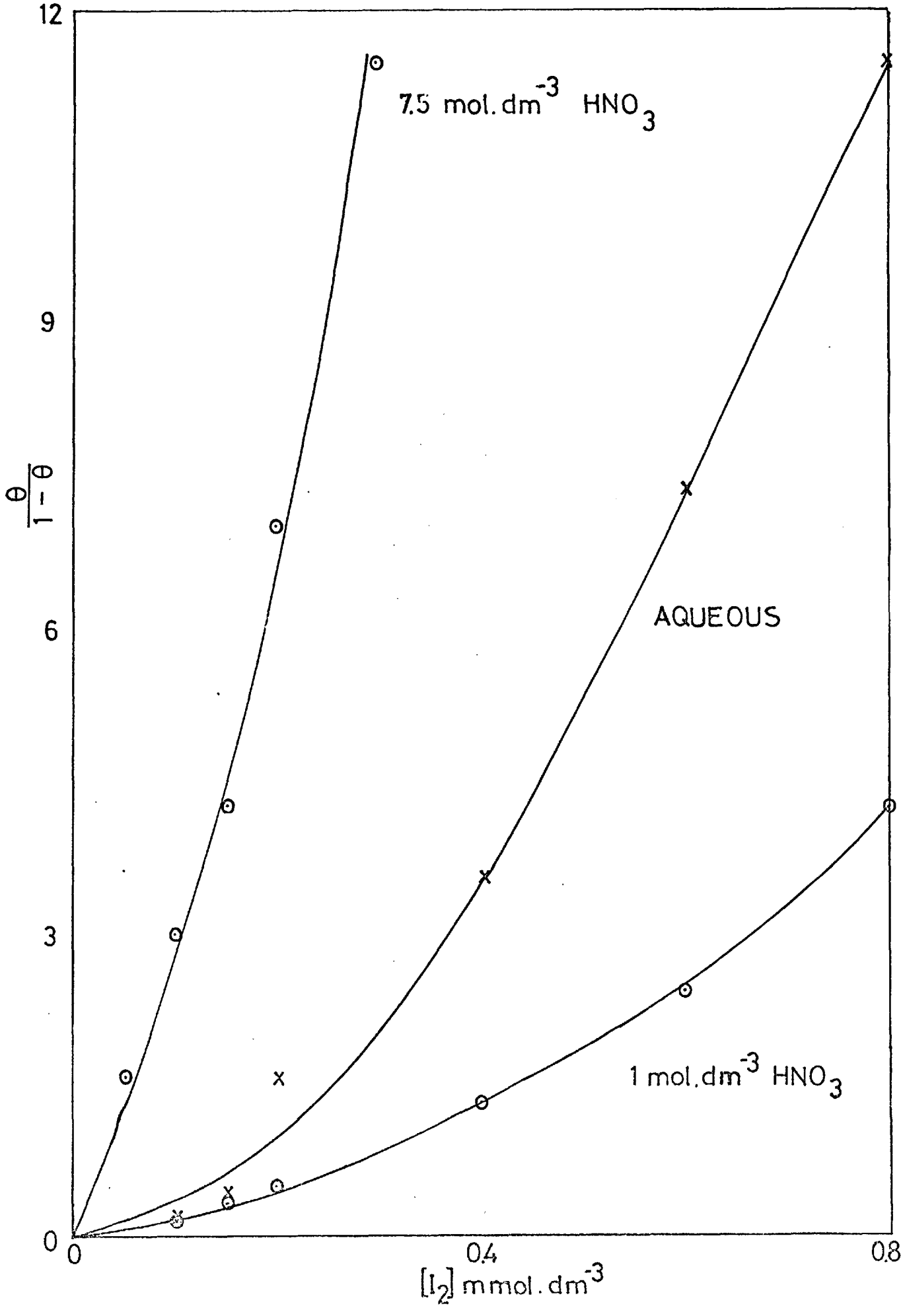
GRAPH 4.16

FREUNDLICH ISOTHERM PLOT OF EQUILIBRIUM CONCENTRATIONS OF IODINE IN SOLUTION ($\bar{m}$. mol. dm^{-3}) AND ON THE RESIN (m. mol. dm^{-3}) IN 7.5 mol. dm^{-3} NITRIC ACID SOLUTION



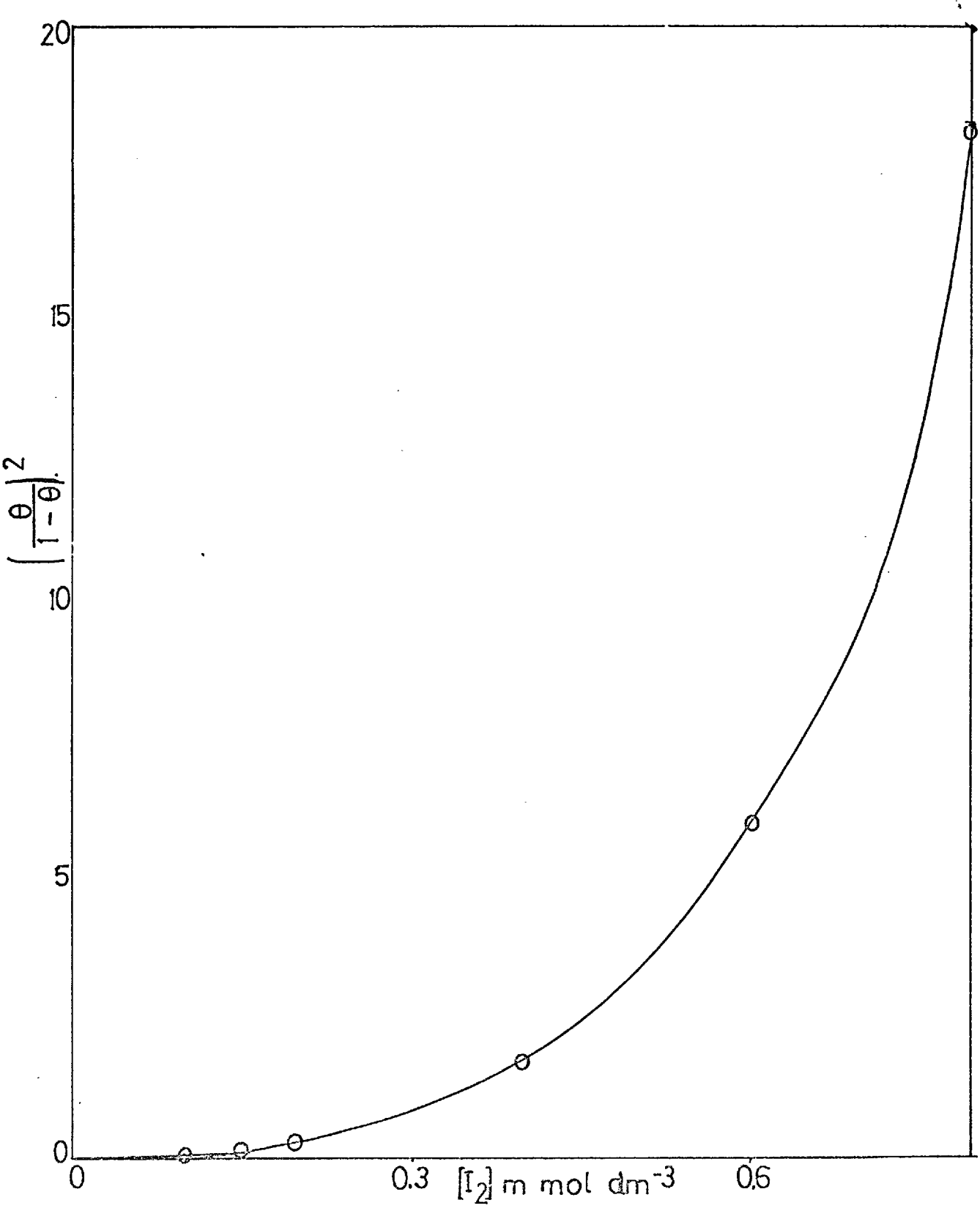
GRAPH 4.17

LANGMUIR ISOTHERM PLOT OF EQUILIBRIUM CONCENTRATION OF IODINE IN SOLUTION (m.mol. dm^{-3}) VERSUS THE FUNCTION ($\theta/1-\theta$) AT DIFFERENT ACID CONCENTRATIONS

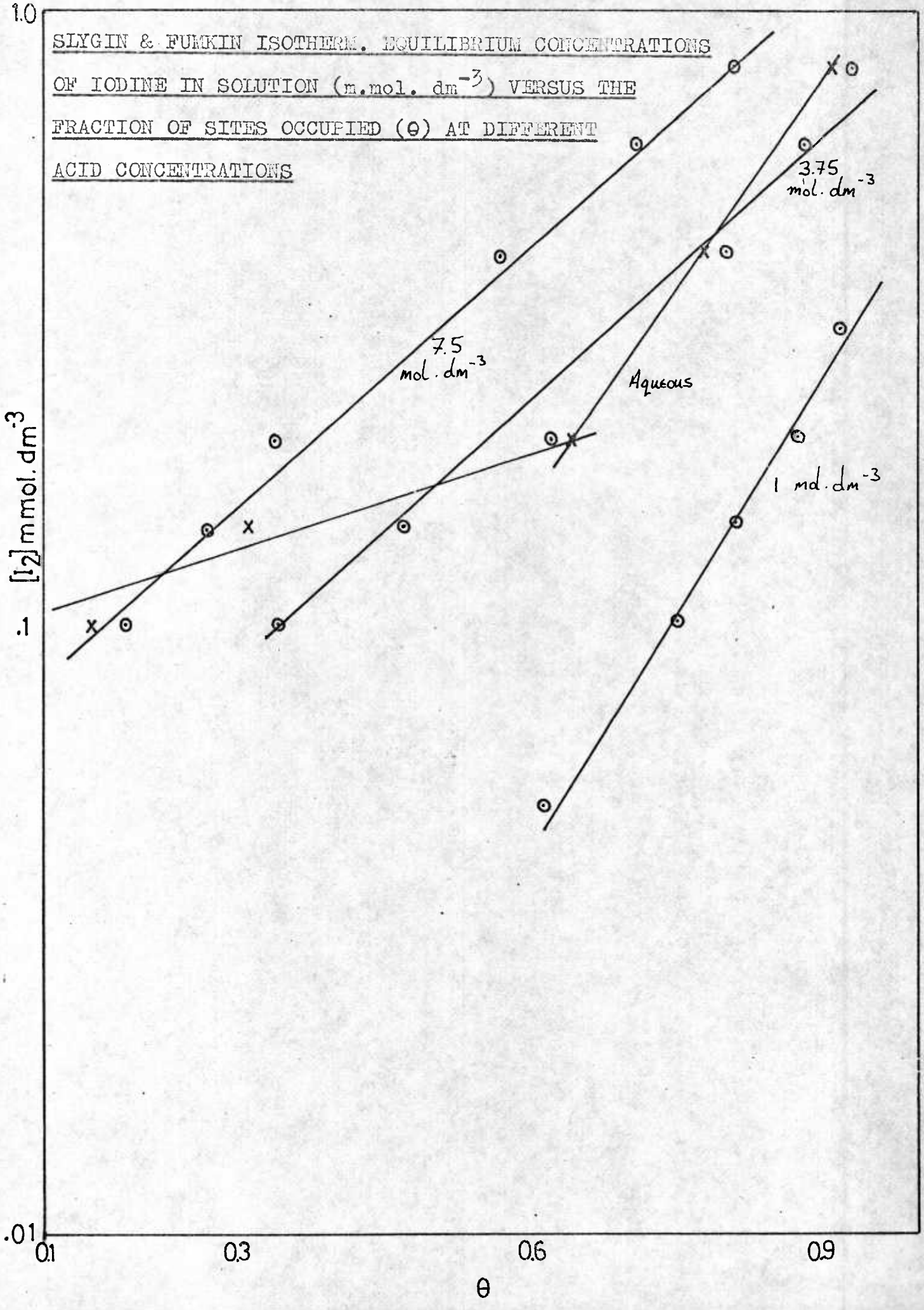


GRAPH 4.18

LANGMUIR WITH DISSOCIATION PLOT FOR 1 mol. dm^{-3} NITRIC ACID CONCENTRATION



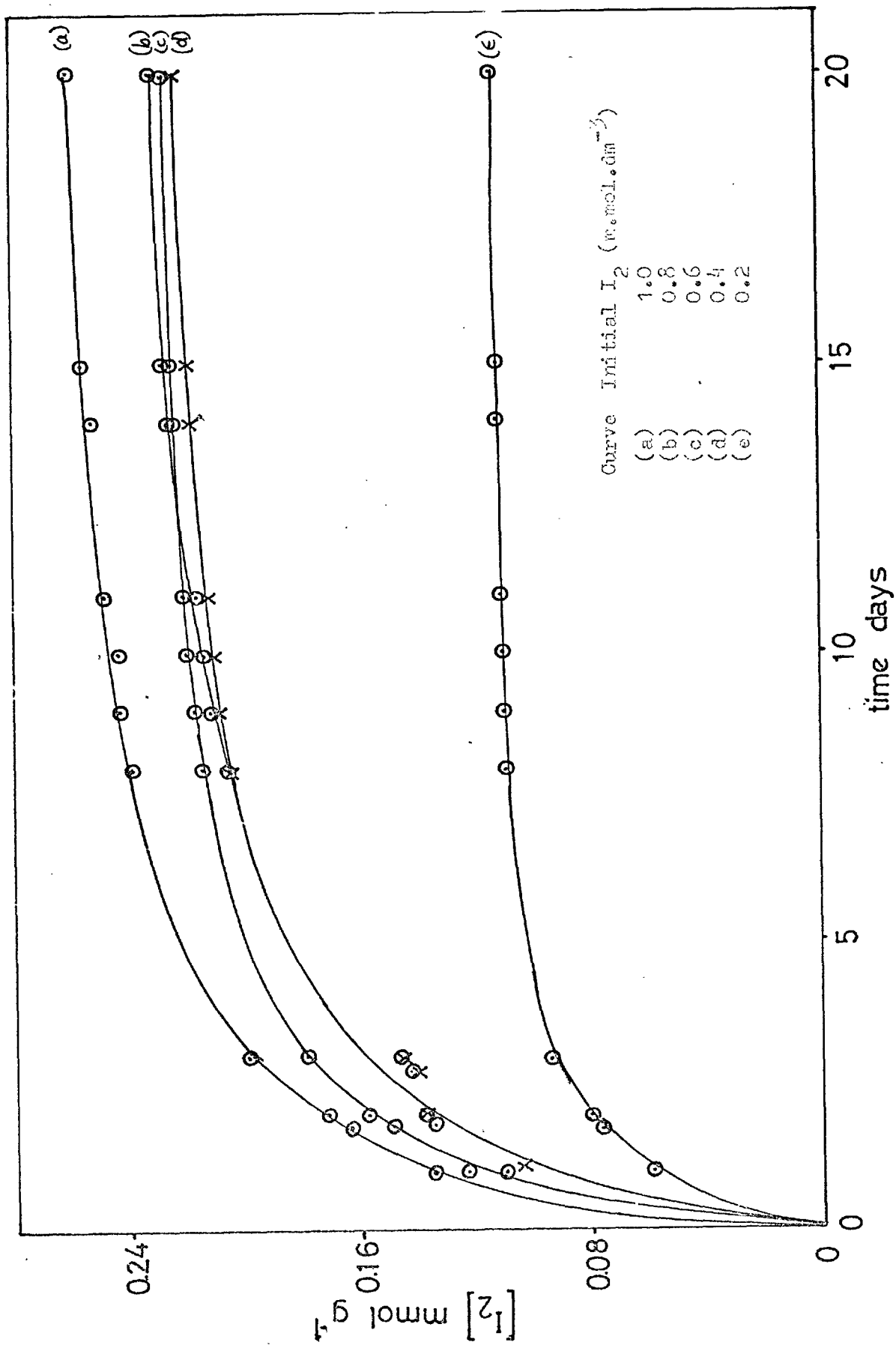
GRAPH 4.19


SLYGIN & FUMKIN ISOTHERM. EQUILIBRIUM CONCENTRATIONS OF IODINE IN SOLUTION (m.mol. dm^{-3}) VERSUS THE FRACTION OF SITES OCCUPIED (θ) AT DIFFERENT ACID CONCENTRATIONS
1.0
.1
.01
[I2] m mol. dm^{-3}
0.1
0.3
0.6
0.9
θ
7.5 mol. dm^{-3}
3.75 mol. dm^{-3}
Aqueous
1 md. dm^{-3}

GRAPH 4.20

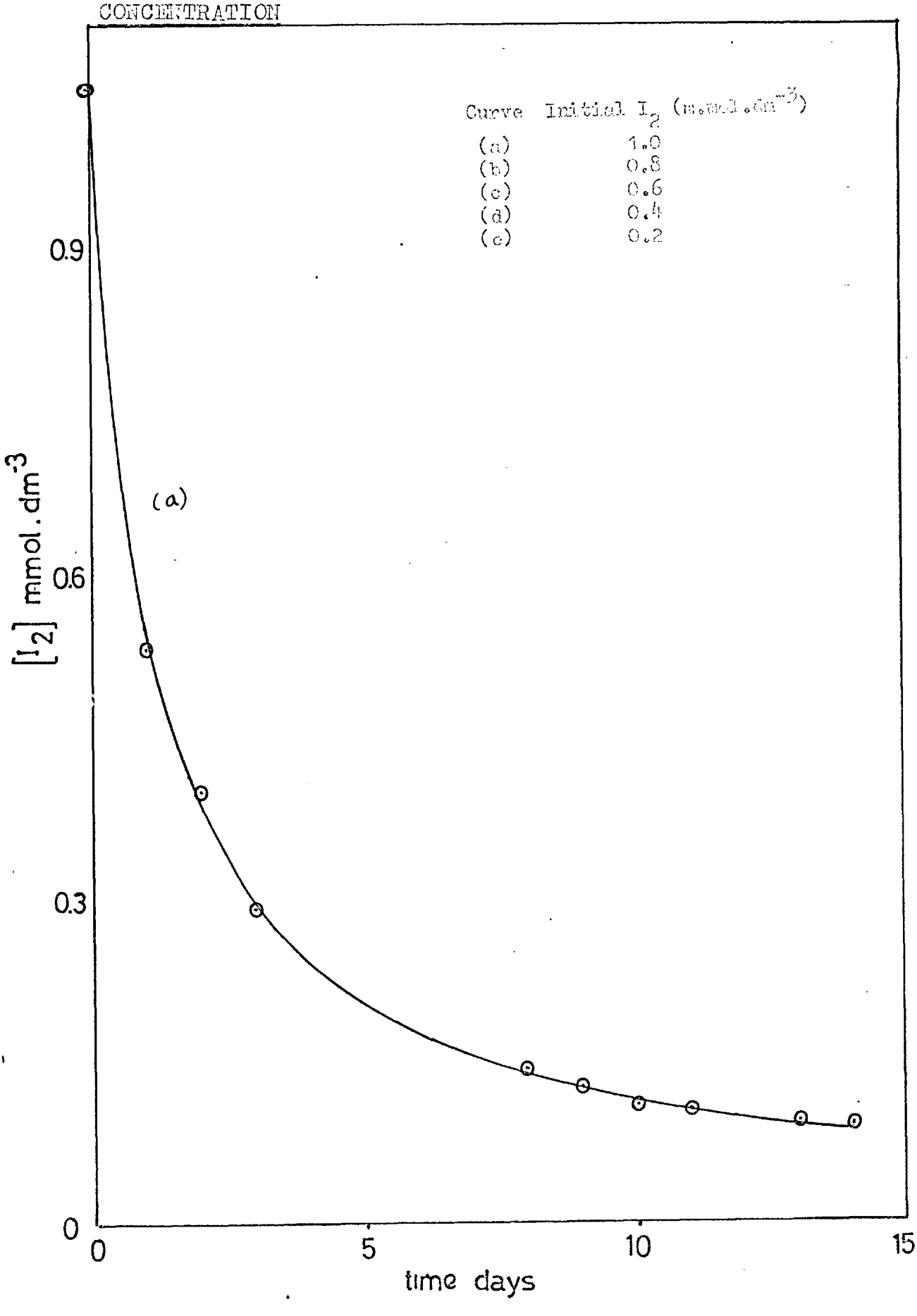
RESIN CONCENTRATION (m.mol. g^{-1}) VERSUS TIME (days),

7.5 mol.dm^{-3} NITRIC ACID SOLUTION, RESIN XAX 1285



GRAPH 4.21

TYPICAL PLOT OF IODINE SOLUTION CONCENTRATION (m.mol. dm^{-3}) VERSUS TIME, USED FOR CALCULATING THE RATE OF CHANGE OF CONCENTRATION

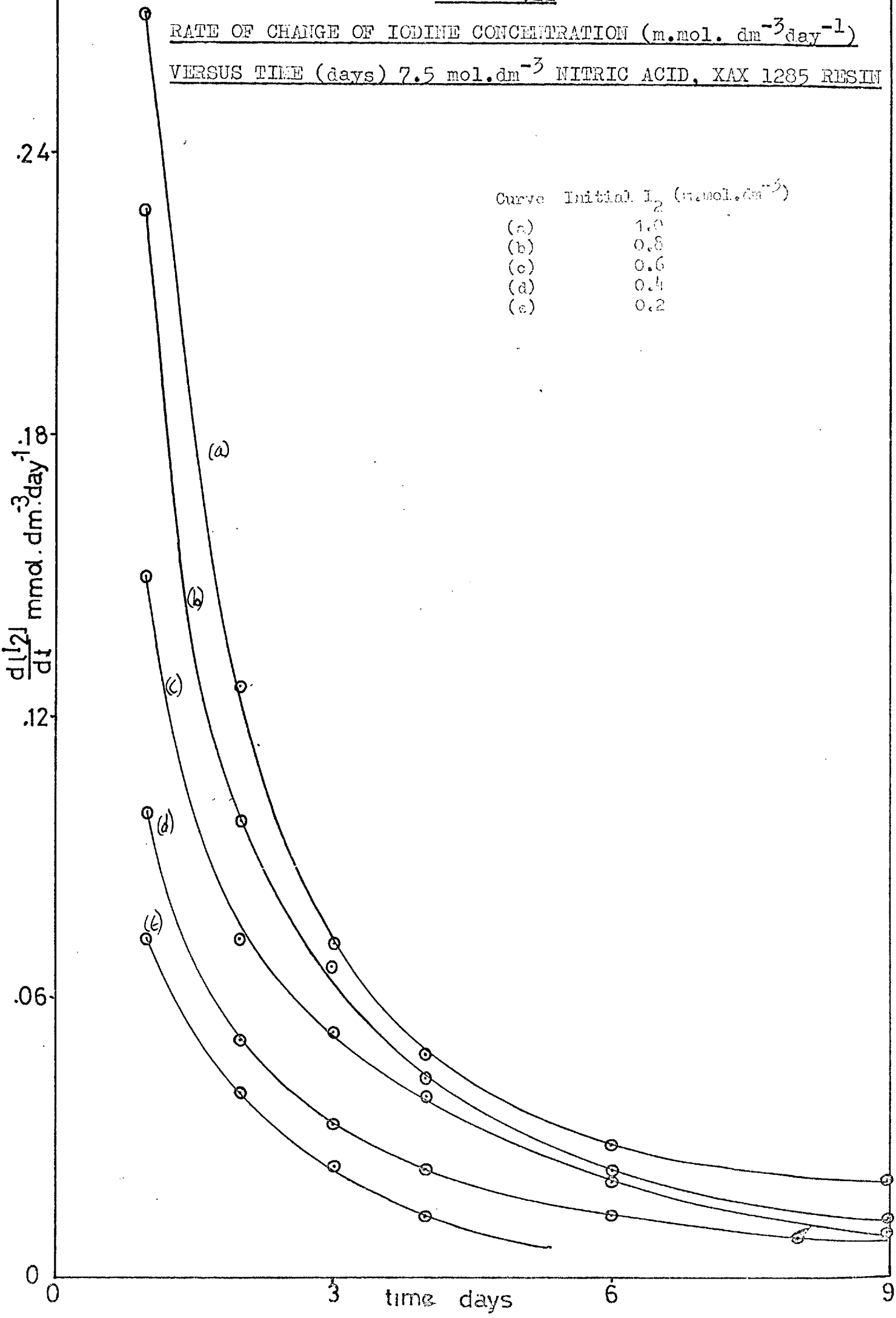


GRAPH 4.22

RATE OF CHANGE OF IODINE CONCENTRATION (m.mol. $dm^{-3}day^{-1}$)

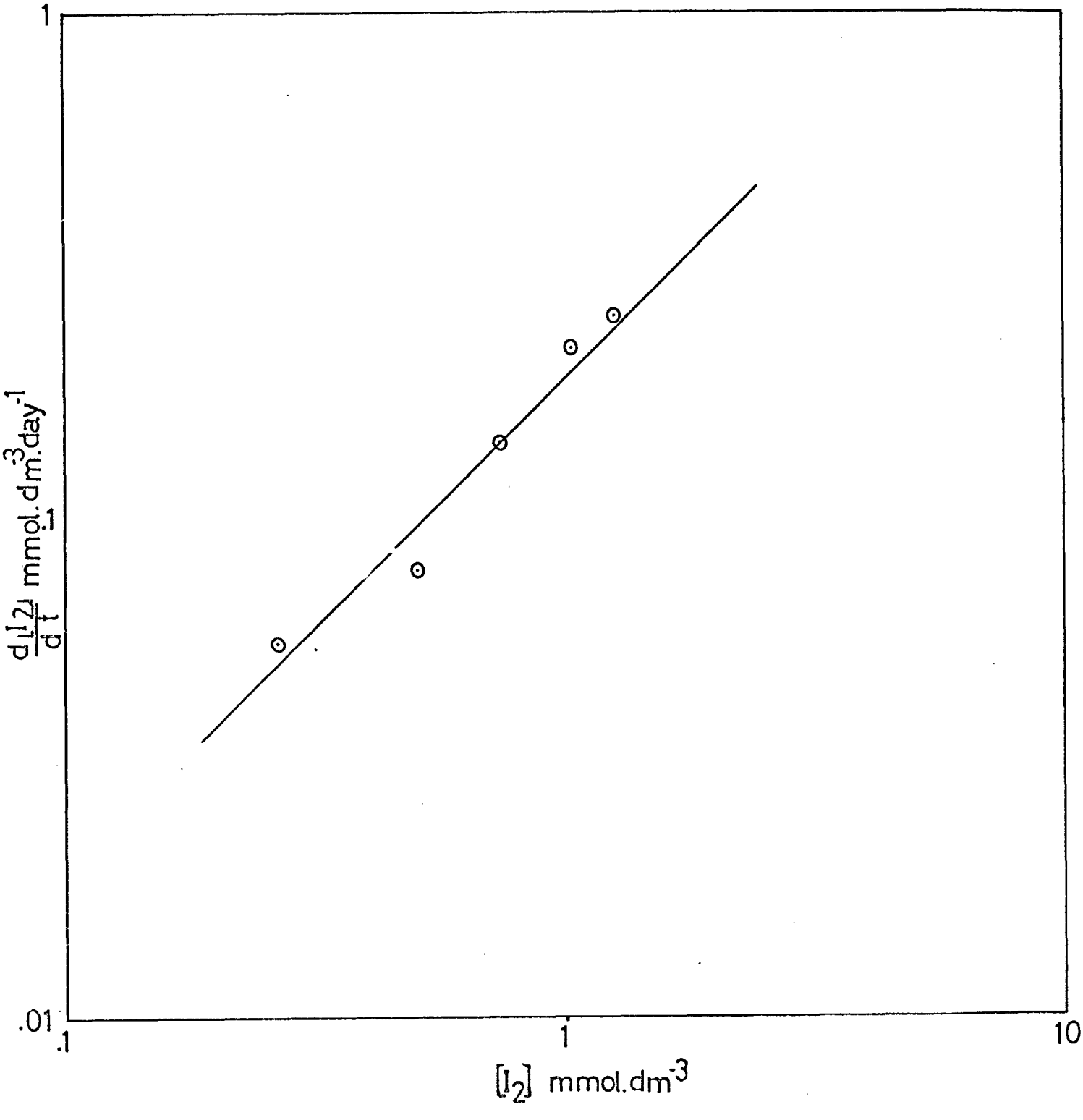
VERSUS TIME (days) 7.5 mol.dm^{-3} NITRIC ACID, XAX 1285 RESIN

Curve	Initial I_2 (m.mol.dm^{-3})
(a)	1.0
(b)	0.8
(c)	0.6
(d)	0.4
(e)	0.2



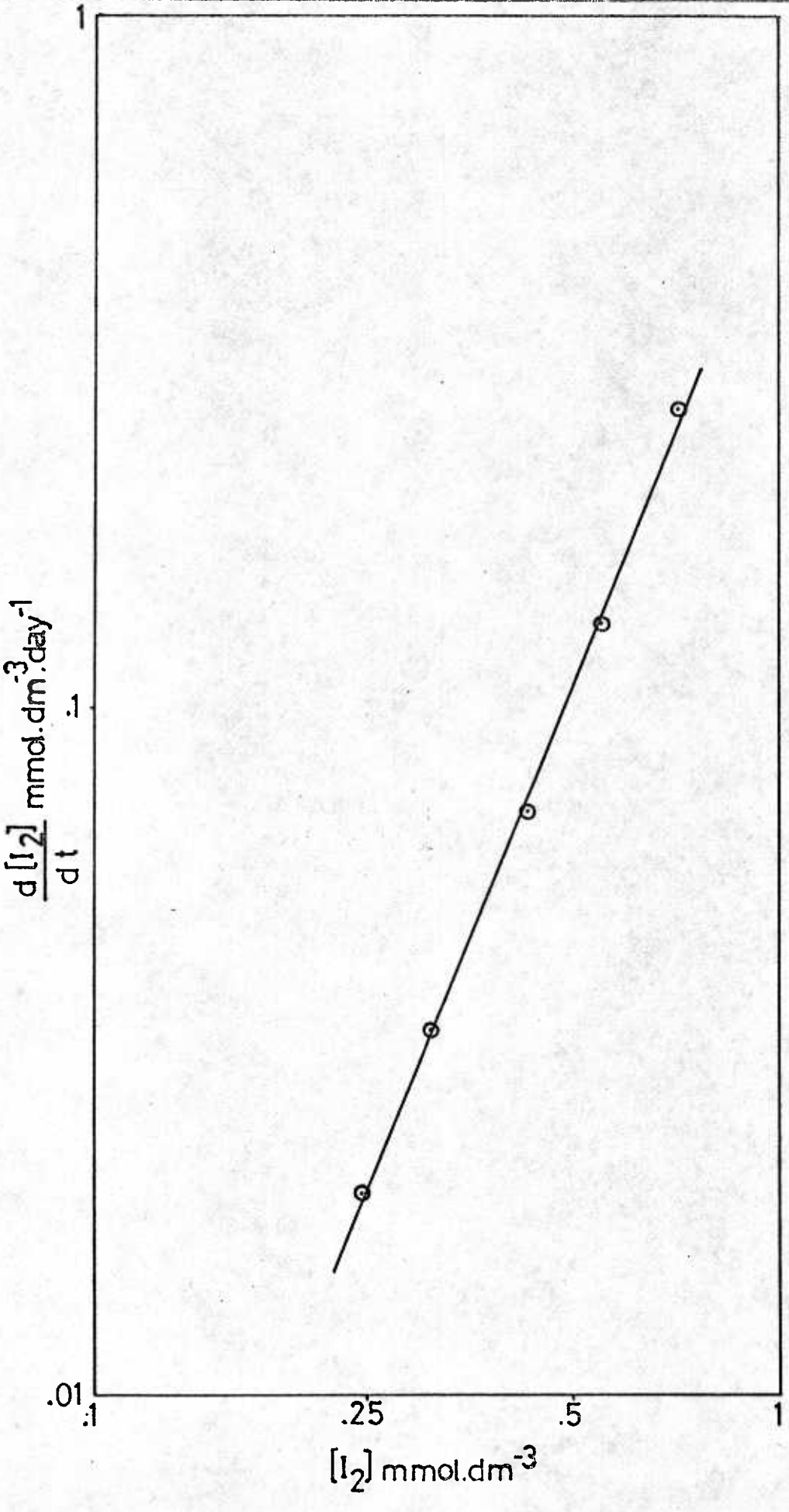
GRAPH 4.23

INITIAL RATE OF DECREASE OF IODINE IN SOLUTION (m.mol. dm^{-3} day^{-1}) VERSUS INITIAL IODINE CONCENTRATION IN SOLUTION (m.mol. dm^{-3}). RESIN XAX 1285, 7.5 mol. dm^{-3} NITRIC ACID



GRAPH 4.24

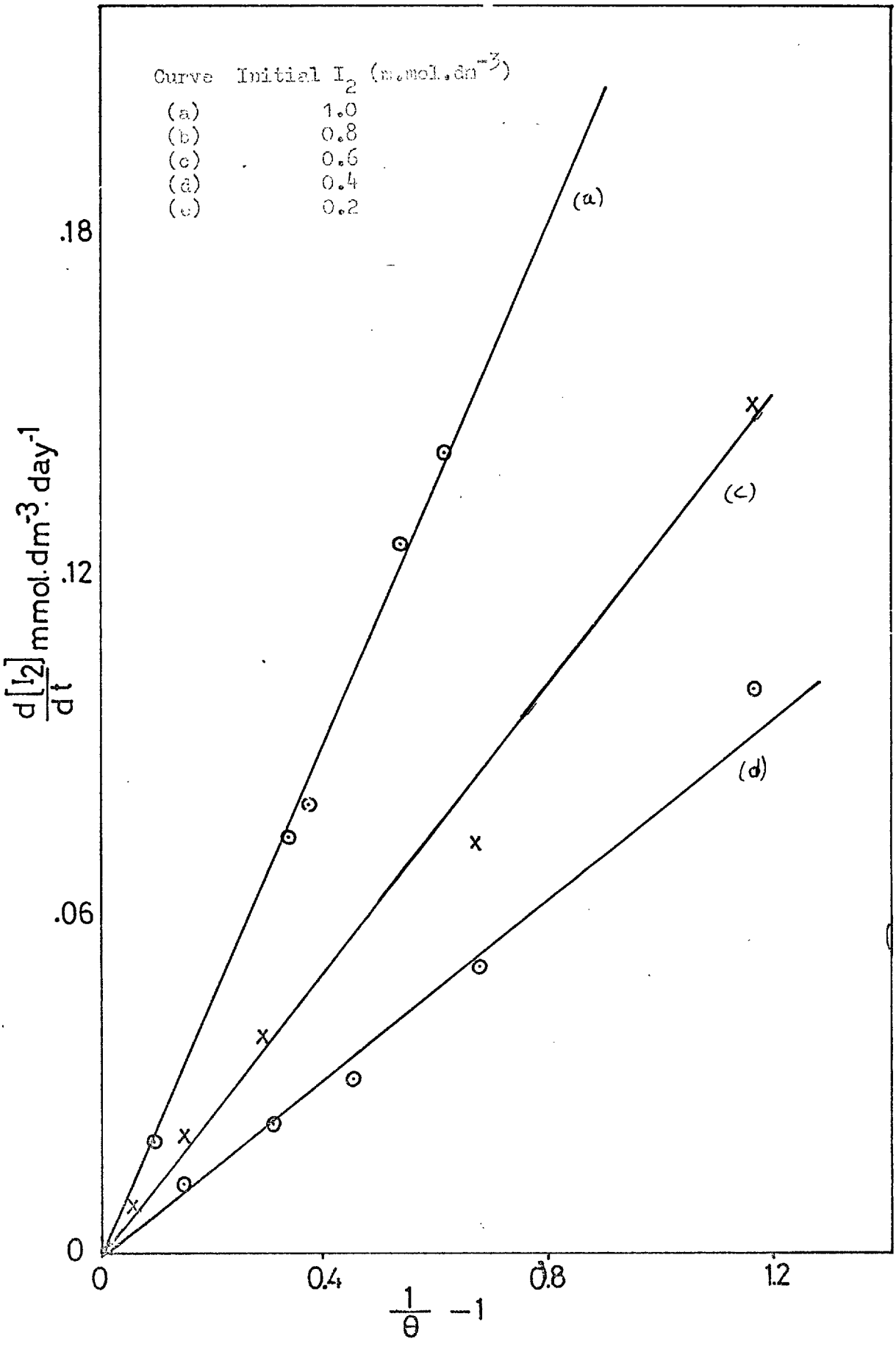
RATE OF DECREASE OF IODINE IN SOLUTION (m.mol. dm^{-3} day^{-1}) VERSUS IODINE CONCENTRATION (m.mol. dm^{-3}) FOR A SINGLE EXPERIMENT. RESIN XAX 1285, 7.5 mol. dm^{-3} NITRIC ACID



GRAPH 4.25

INVERSE DRIVING FORCE ISOTHERM. RATE OF UPTAKE OF IODINE FROM SOLUTION (m.mol. dm^{-3} day^{-1}) VERSUS $(\frac{1}{\theta} - 1)$.

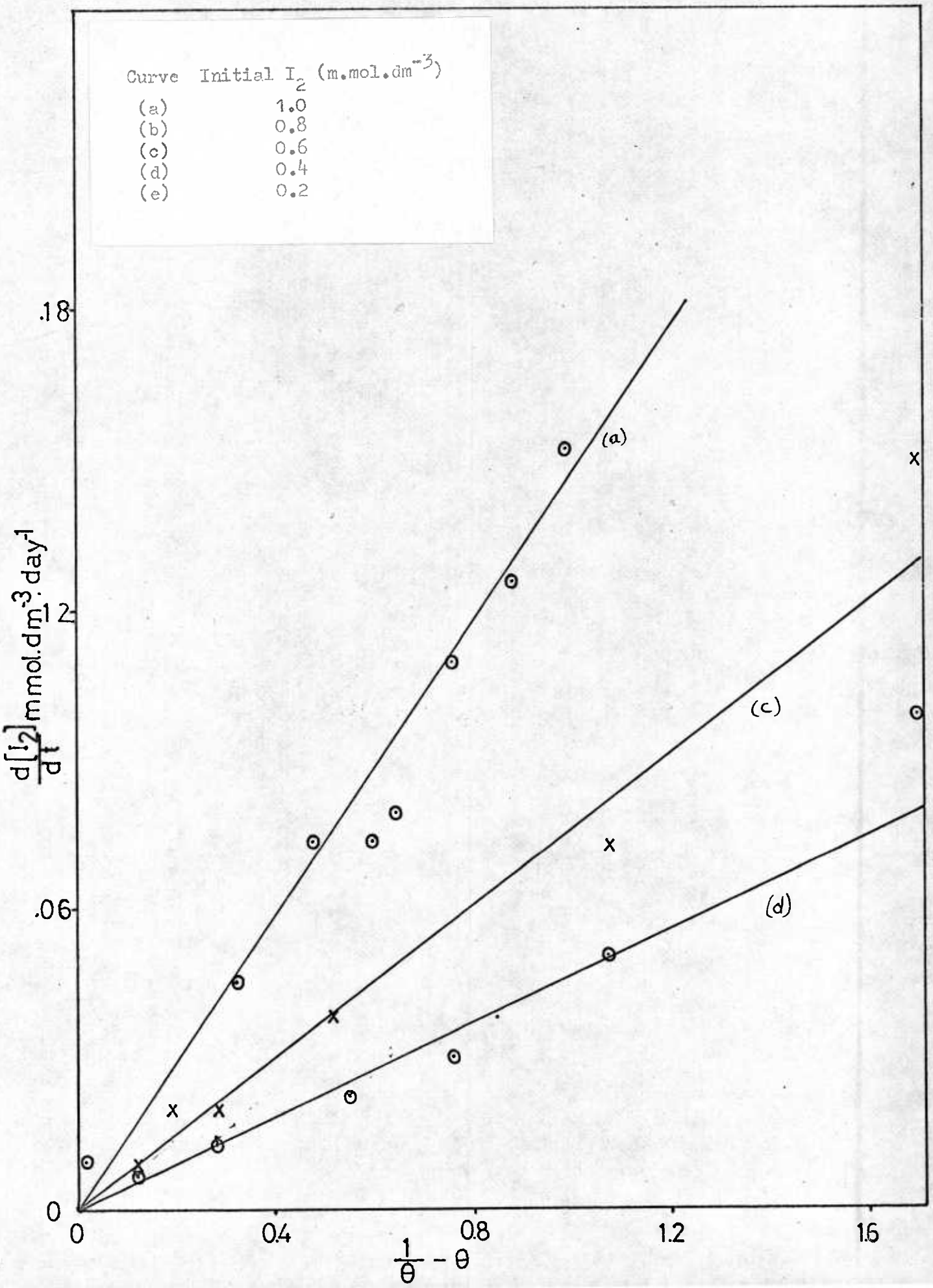
DATA FROM GRAPH 4.22



GRAPH 4.26

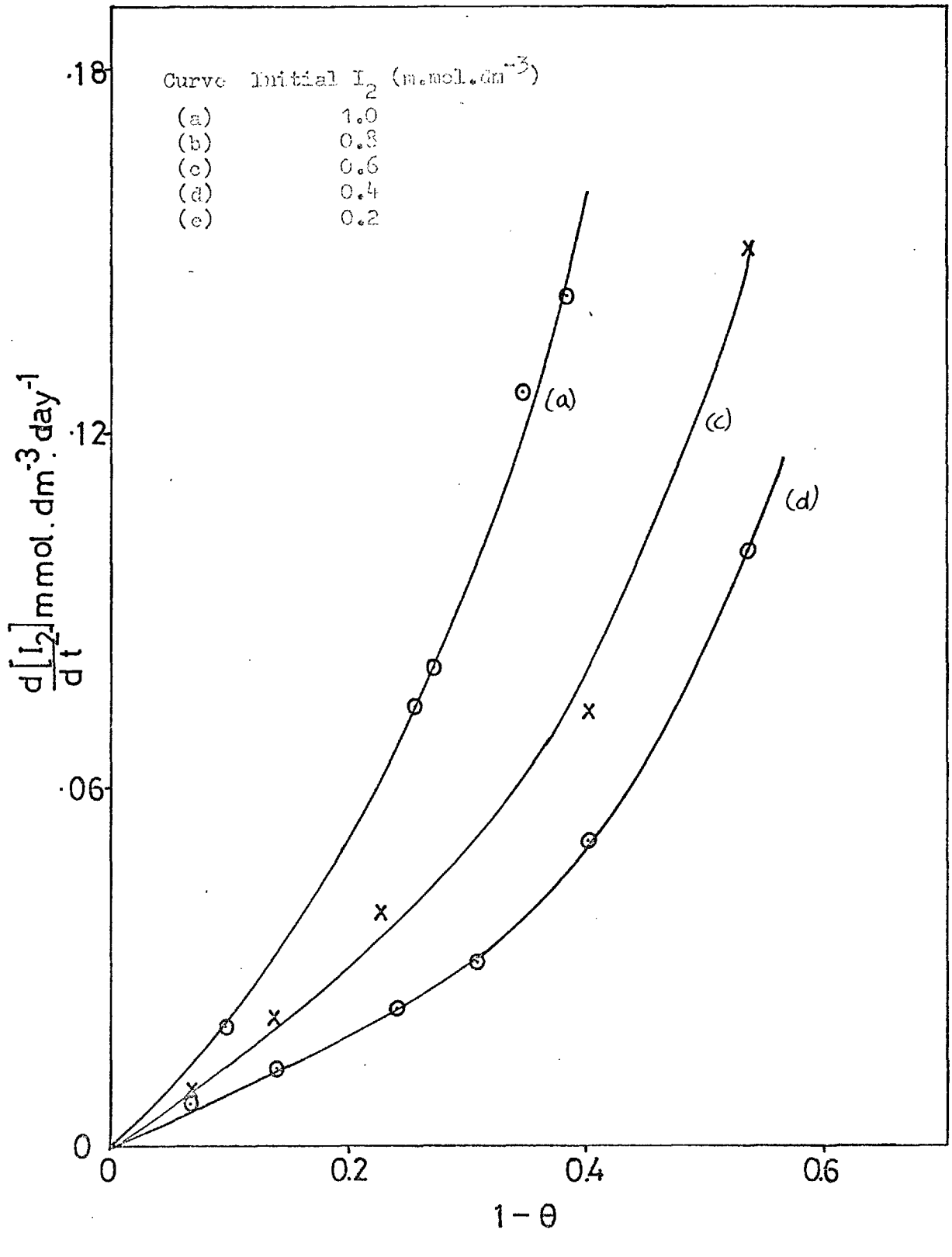
QUADRATIC DRIVING FORCE ISOTHERM. RATE OF UPTAKE OF IODINE FROM SOLUTION (m.mol. dm^{-3} day^{-1}) VERSUS $(\frac{1}{\theta} - \theta)$.

DATA FROM GRAPH 4.22



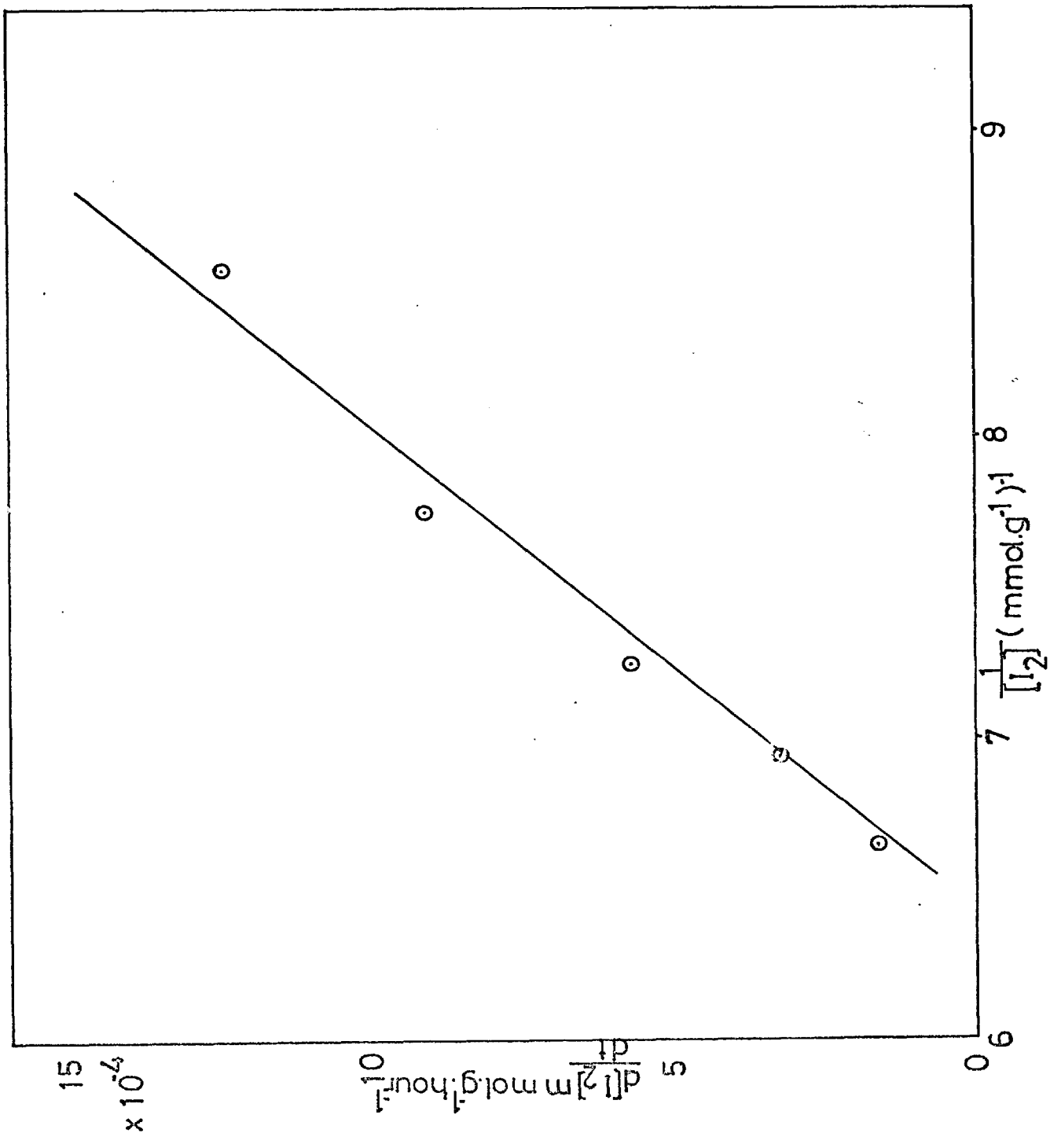
GRAPH 4.27

LINEAR DRIVING FORCE ISOTHERM. RATE OF UPTAKE OF IODINE FROM SOLUTION (m.mol. $dm^{-3}day^{-1}$) VERSUS DATA FROM GRAPH 4.22



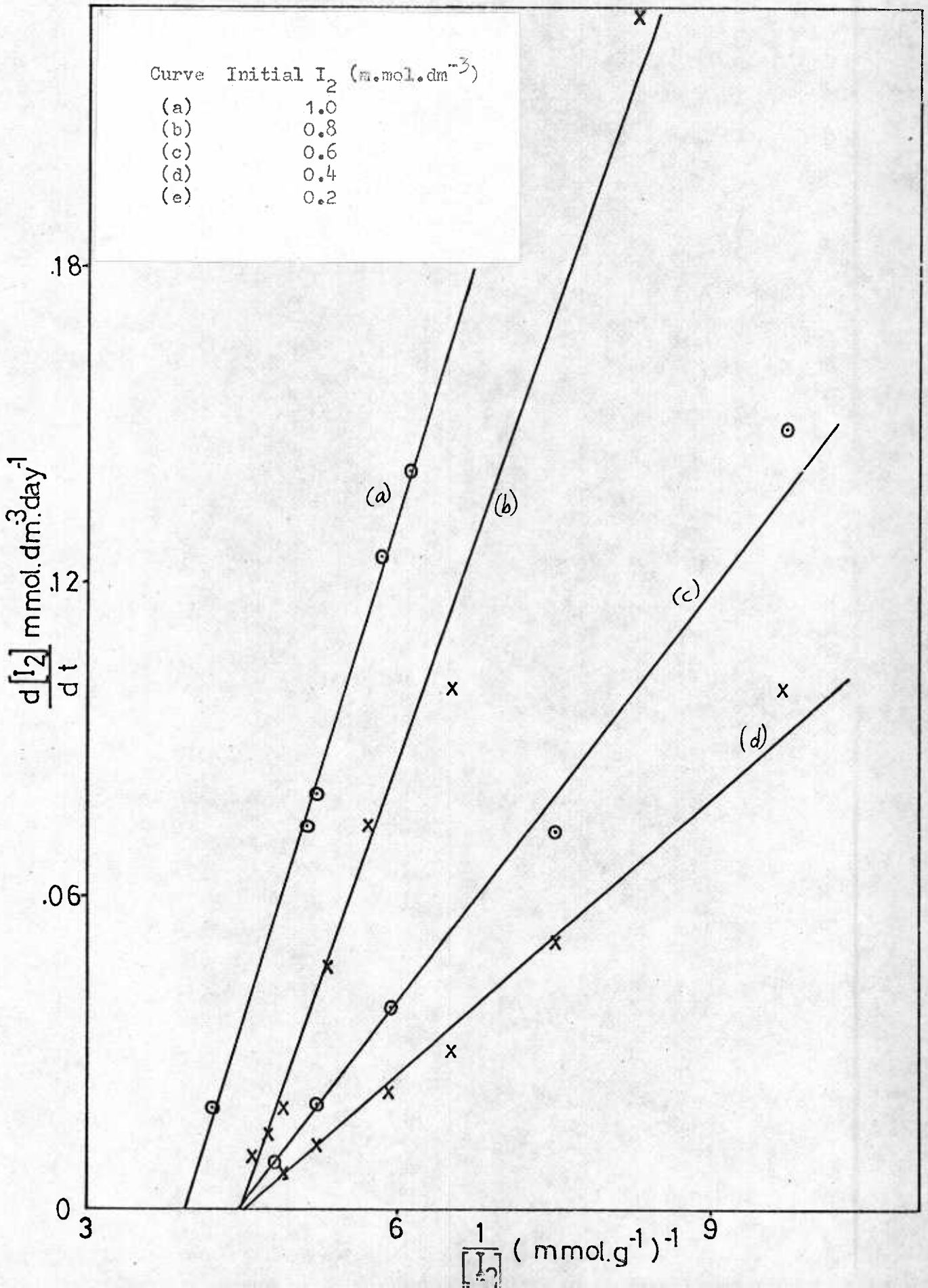
GRAPH 4.28

RATE OF UPTAKE OF IODINE (m.mol. g^{-1} $hour^{-1}$) FROM AQUEOUS SOLUTION ON TO POLYSTYRENE BEADS (8% D.V.B. ADDED) VERSUS 1/IODINE CONCENTRATION ON THE BEADS



GRAPH 4.29

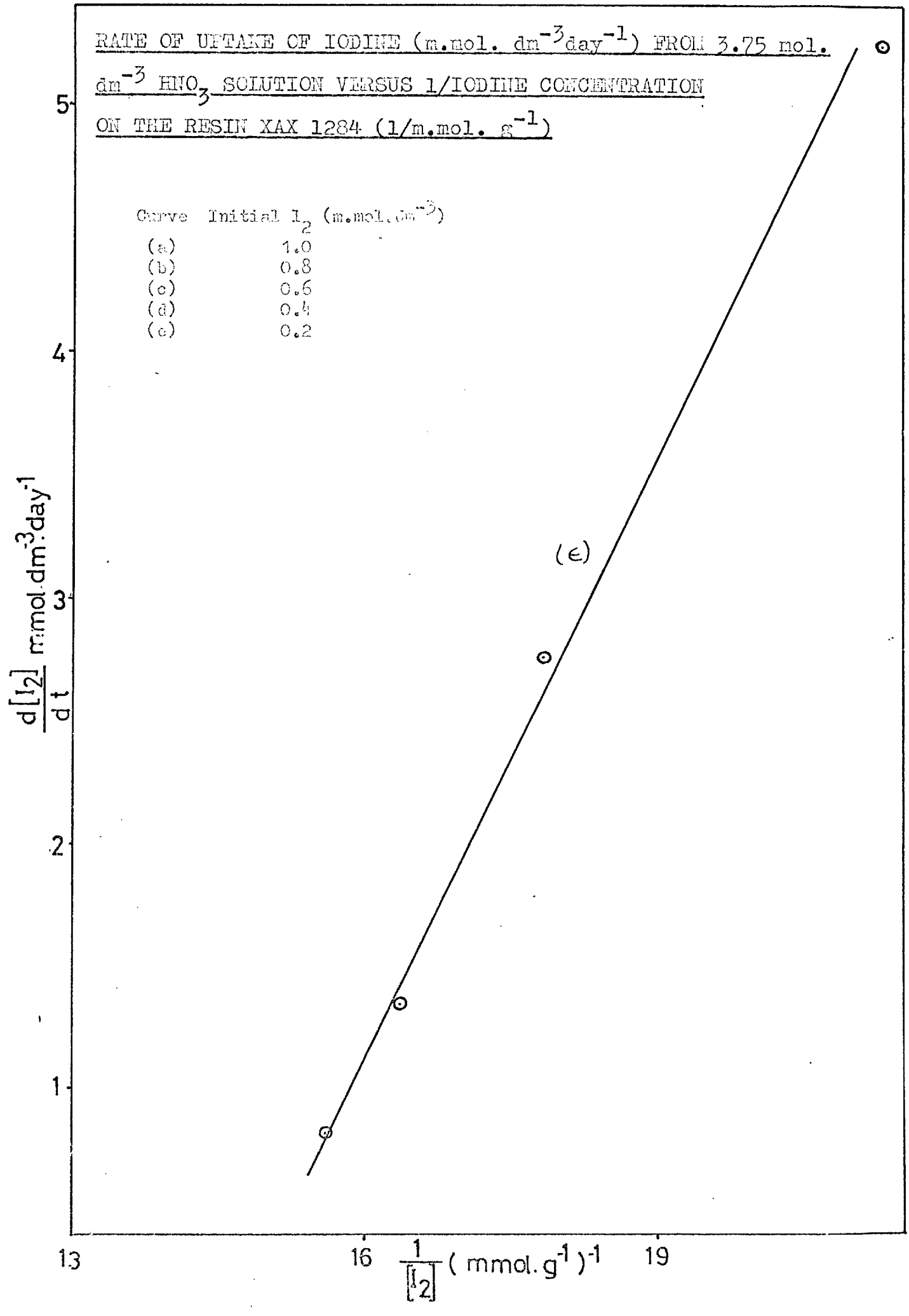
RATE OF UPTAKE OF IODINE (m.mol. dm^{-3} day^{-1}) VERSUS 1/IODINE ON THE RESIN XAX 1285 (1/m.mol. g^{-1}) IN 7.5 mol. dm^{-3} NITRIC ACID



GRAPH 4.30

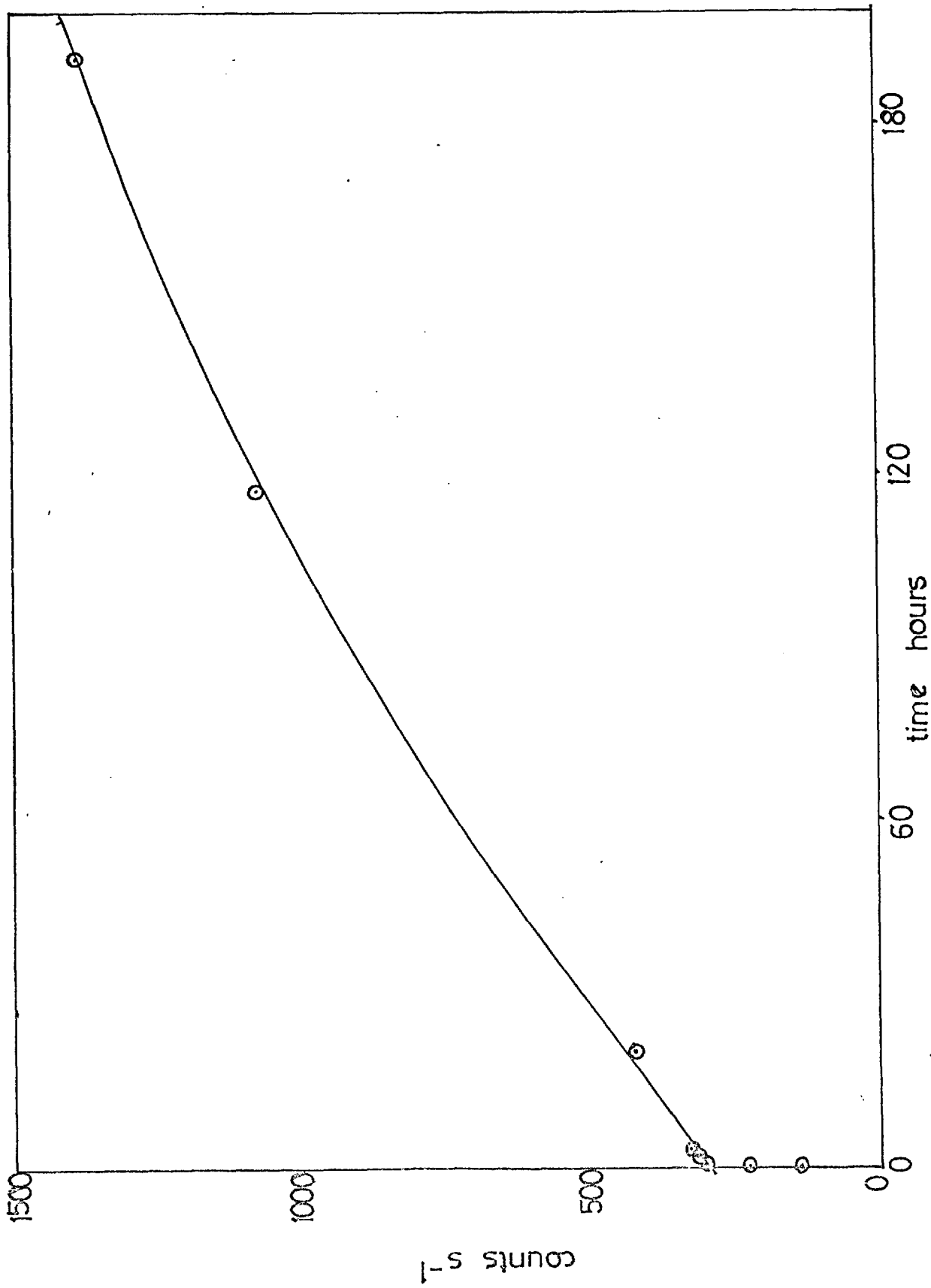
RATE OF UPTAKE OF IODINE (m.mol. $dm^{-3}day^{-1}$) FROM 3.75 mol. dm^{-3} HNO_3 SOLUTION VERSUS 1/IODINE CONCENTRATION ON THE RESIN XAX 1284 (1/m.mol. g^{-1})

Curve	Initial I_2 (m.mol.dm^{-3})
(a)	1.0
(b)	0.8
(c)	0.6
(d)	0.4
(e)	0.2



GRAPH 4.31

ELUTION OF AN AQUEOUSLY LOADED SAMPLE. TOTAL SOLUTION ACTIVITY (s^{-1}) VERSUS TIME (hours)



UPTAKE OF IONIC IODINE SPECIES BY ION EXCHANGE RESINS

SECTION FIVE

5. UPTAKE OF IONIC IODINE SPECIES BY ION EXCHANGE RESINS

5.1. INTRODUCTION

It has already been shown (section one) that iodine is important in nuclear technology. Molecular iodine is by far the most important species although other ionic species may exist and thus require consideration.

In nuclear fuel reprocessing, iodate and periodate species could be fairly important. In water cooled reactor circuits, iodides could well be released by accidental rupture of a fuel can.

The purpose of this section is therefore to consider the likely behaviour of these ionic species in the presence of ion exchange resins.

5.2. UPTAKE OF IODATE BY XAX RESINS

5.2.1. Experimental Methods

Simple batch experiments were carried out as before. An iodate tracer, labelled with iodine-125, was used to determine the iodate concentration in solution. Labelled iodate was unobtainable and hence it was prepared from a labelled potassium iodide solution (161).

5.2.2. Production of Iodine-125 Labelled Iodate Solutions

A labelled potassium iodide solution, code no. IMS.3, was purchased from the Radiochemical Centre, Amersham. To this ~~was~~ were added 10 mg. of inactive potassium iodide and 1.5 cm^3. saturated solution of barium chlorate. This mixture was heated to 353 ^oK, and a mixture of 0.2 cm^3. 10% sodium nitrite solution and 0.2 cm^3. 5 mol. dm^{-3}. nitric acid solution was added. A precipitate of barium iodate was formed. The solution was maintained at 353 ^oK for a further five minutes and then cooled in ice for one hour. The barium iodate was centrifuged off and washed with five

aliquots of 0.2 cm^3. deionised water. This precipitate was suspended in water containing 5.3 mg. of potassium sulphate (total volume 3 cm^3.). This mixture was then heated on a water bath for thirty minutes, with occasional stirring. The barium sulphate precipitate was centrifuged off leaving a labelled potassium iodate solution.

5.2.3. Uptake from Aqueous Solution onto XAX Resins

No iodate could be taken onto the resin by an ion exchange reaction whilst the latter was in the freely basic form. Also it appeared that no detectable adsorption of iodate occurred.

5.2.4. Uptake from Nitric Acid Solutions onto XAX Resins

Solutions of potassium iodate, concentration circa 10^{-3} mol. dm^{-3}, were used as this represented the maximum possible iodine concentration likely to be present in a dissolver solution (section one).

(a) From 1 mol. dm^{-3} HNO_3

The uptake onto XAX resins (1283, 1284 and 1285) at these concentrations was so low as to be almost undetectable. Maximum loading obtained was 0.003 m mol. g^{-1} and in this range large analytical inaccuracies can occur (appendix two).

(b) From 7.5 mol. dm^{-3} HNO_3

Graph 5.1 illustrates equilibrium curves for XAX 1284 and XAX 1285. The iodine uptake was much greater than that from 1 mol. dm^{-3} HNO_3 solution. Also the uptake was greater onto the more highly crosslinked resin (see also graph 5.2).

Increase in the nitric acid concentration must have affected either the resin, or the iodate within the pore solution of the resin, since iodate is perfectly stable at this external concentration of nitric acid.

The acid concentration within the resin, however, will be considerably more concentrated than that in the solution (156). It is therefore possible that oxidation of the iodate could take place inside the resin leading to the formation of iodine species, e.g. periodates, which were more selectively taken up onto the resin. This theory was given further substance by the effect of crosslinking on the equilibrium. The more highly crosslinked the resin, the less it swells and the higher is the activity of the nitric acid within the pores. If iodate was being oxidised by nitric acid, therefore, a higher degree of crosslinking would enhance this effect. Consequently, the capacity for iodate at this acid concentration should increase with increasing crosslinking. This effect was observed (graphs 5.1, 5.2).

Graph 5.2 illustrates that the approach to equilibrium was slow. In dilute solutions with no agitation, a film diffusion controlled ion exchange mechanism would be expected (162). A simple check can be made using equation 6.23 of reference 162, to calculate the half time of ion exchange for the case of infinite solution volume.

$$t_{1/2} = 0.23 \frac{r_o \delta \bar{c}}{Dc} \qquad (6.23)$$

where r = radius of bead 0.05 cm

c = solution concentration 10^{-3} mol. $dm.^{-3}$ for IO_3^-

$\bar{c}$ = resin capacity 2 mol. $dm.^{-3}$ for IO_3^-

δ = film thickness estimated as 5×10^{-3} cm.

D = diffusion coefficient estimated as approximately 10^{-6}

then half time for ion exchange, $t_{1/2}$ = approximately 30 hrs. This value compares reasonably with that obtainable from graph 5.2. (approximately 12 - 24 hours).

5.2.5. Consequences of the Iodate Results for an Envisaged Fuel Reprocessing cycle

In such a cycle, plutonium would be loaded from 7.5 mol. dm^{-3} nitric acid solution (approx.) and eluted with 1 mol. dm^{-3} nitric acid solution. Unfortunately iodate would tend to follow the plutonium leading to contamination of the purified solutions.

5.3. UPTAKE OF IODIDE BY XAX RESINS

A small amount of work was carried out on aqueous iodide solutions. It is impossible for iodide to exist in a nitric acid dissolver solution in an ionic form as it would be rapidly oxidised to elemental iodine. However, it is possible that ionic iodides could occur in a coolant circuit of a water reactor. Some work was carried out with the weakly basic resins in order to obtain further insight into the behaviour of such resins in aqueous solutions.

5.3.1. Experimental Methods

Simple batch experiments were carried out as before. A labelled potassium iodide solution (KI^{125}) was used initially. Spectral work was carried out with inactive solutions using a Unicam SP 700 scanning spectrophotometer.

5.3.2. Uptake of Iodide from Aqueous Solution onto Freely Basic Ionac XAX 1284

There was no detectable uptake of iodide onto freely basic resin from aqueous solution. This indicated that there was no detectable adsorption of iodide. Also there was no oxidation of iodide within the resin, otherwise there would have been a large uptake of molecular iodine thus formed.

5.3.3. Uptake of Iodide from Aqueous Solutions onto Nitrate Form Ionac XAX 1284

Graph 5.3 illustrates an uptake curve for iodide onto the nitrate form resin. Considerable adsorption occurred and the most likely explanation is that oxidation of the iodide occurred due to the nitric acid within the pores of the resin. Thus molecular iodine would be formed and consequently strongly adsorbed.

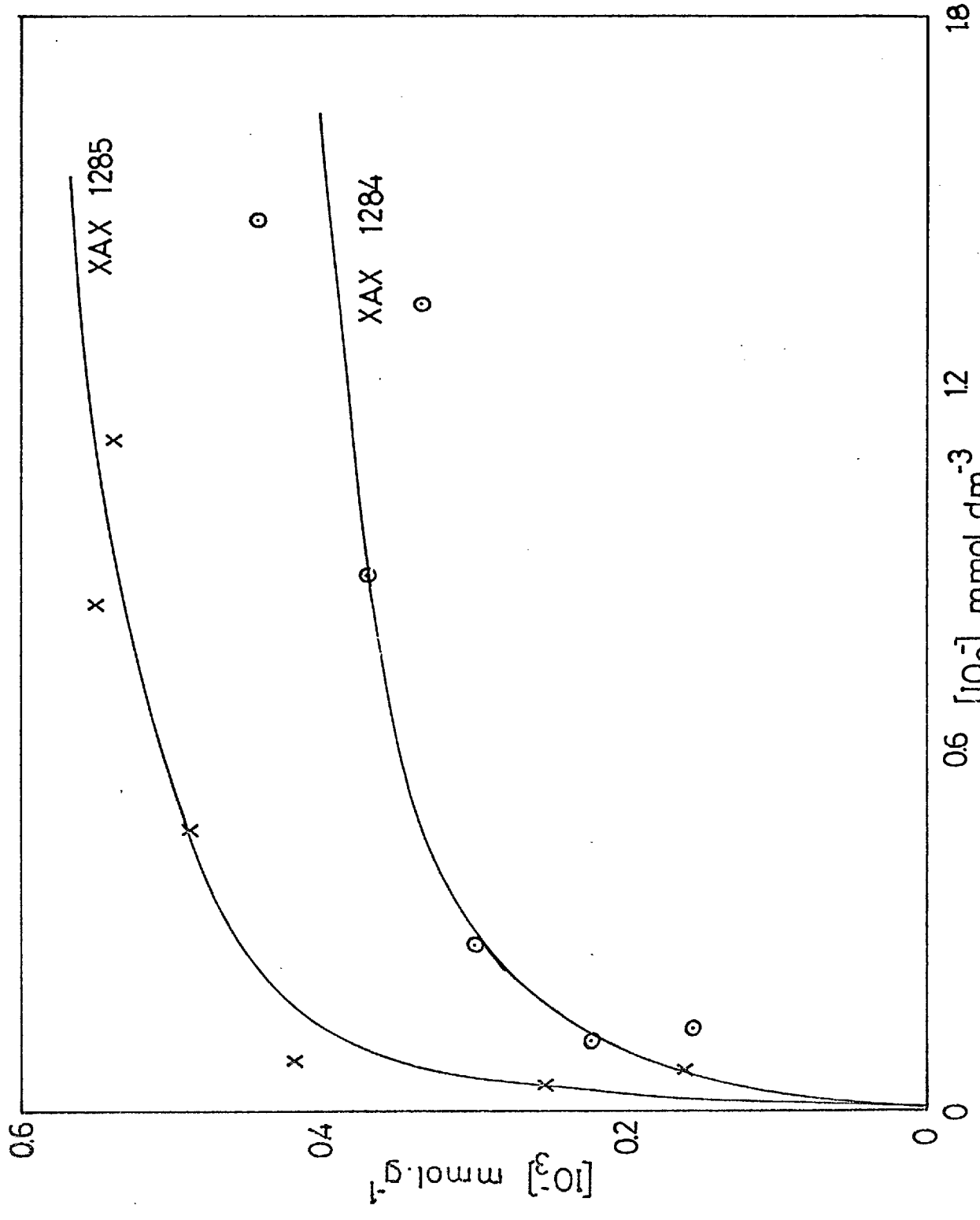
A spectral analysis of a similar solution (graph 5.4) showed that no iodine or I_3^- could be detected in solution although a peak probably due to nitrate was observed at 270 nm. Clearly, hydrolysis of the resin was occurring leading to the formation of nitric acid. This would then oxidise the iodide within the resin and adsorption would occur.

5.3.4. Consequences of the Iodide Results for Coolant Decontamination

If the freely basic form of a vinylpyridine based resin is to be used for decontamination of iodine from aqueous solution, any iodide present could not be taken up onto the resin. However, iodide would be decontaminated by the more conventional resins used in coolant purification (163) and would therefore cause little problem.

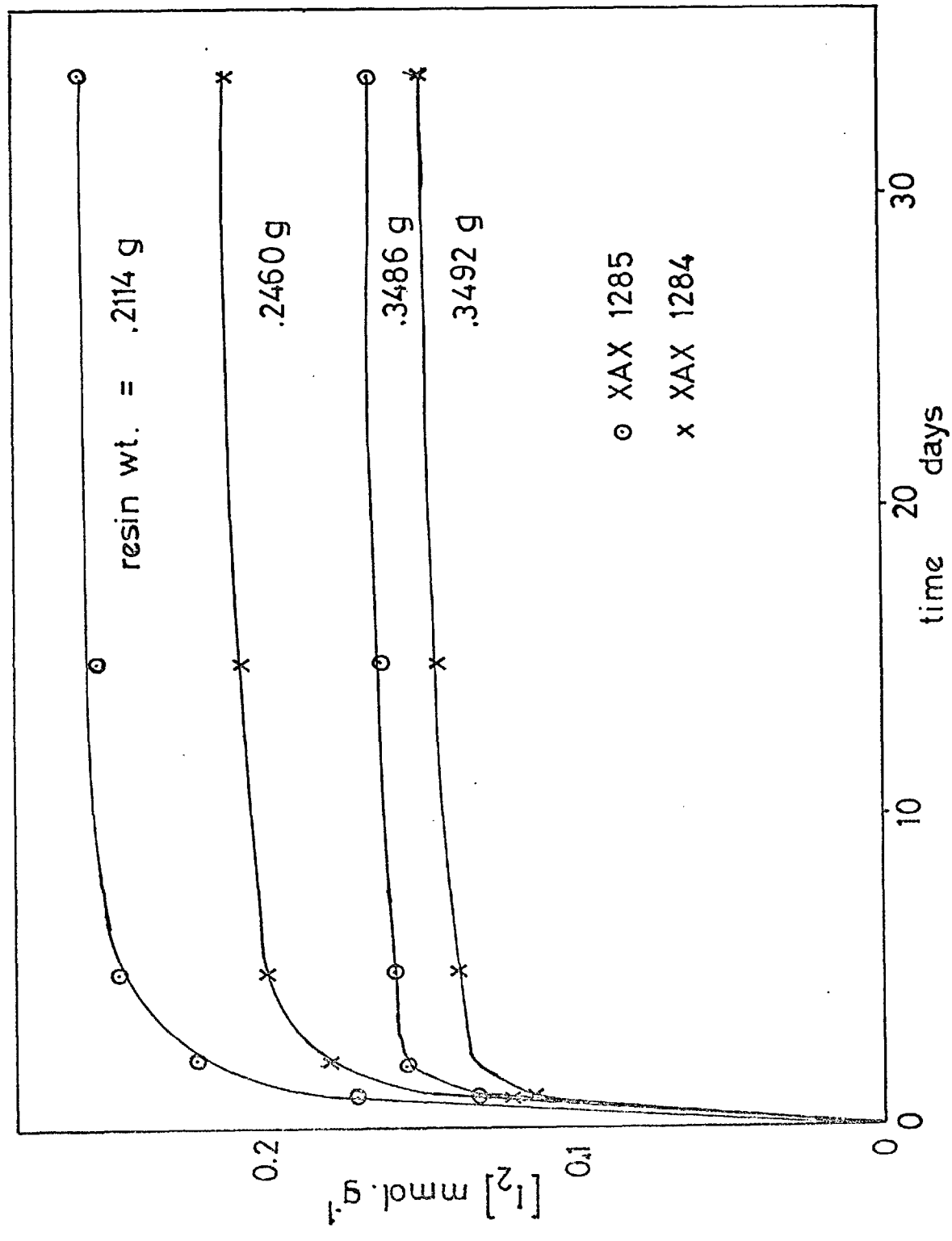
GRAPH 5.1

IODATE EQUILIBRIUM CURVE, RESIN CONCENTRATION (m.mol. g^{-1}) VERSUS SOLUTION CONCENTRATION (m.mol. dm^{-3}), SHOWING THE EFFECT OF CROSSLINKING. EQUILIBRIUM IN 7.5mol. dm^{-3} NITRIC ACID SOLUTION



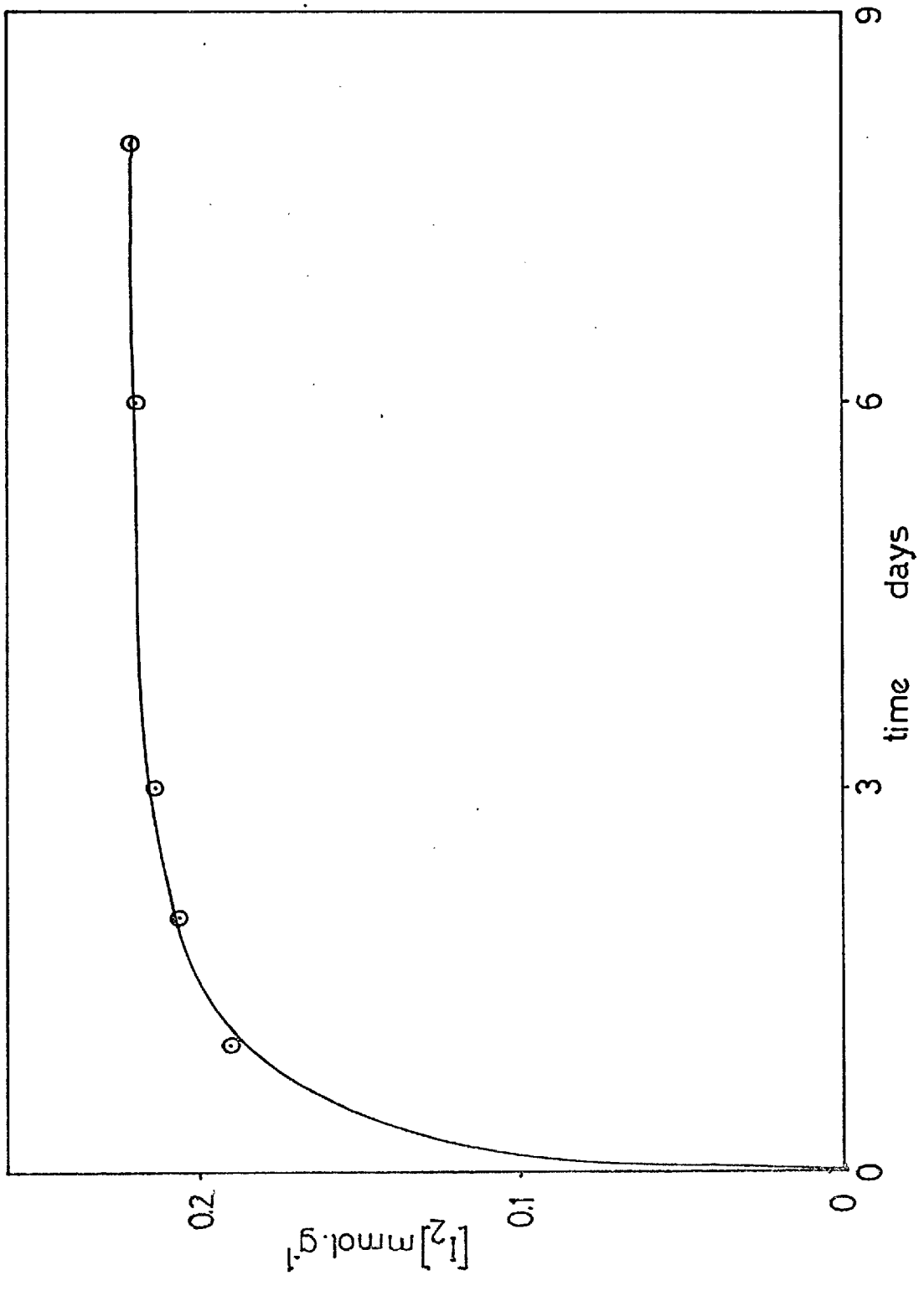
GRAPH 5.2

APPROACH TO EQUILIBRIUM. RESIN CONCENTRATION (n.mol g^{-1}) VERSUS TIME (days), SHOWING THE EFFECT OF CROSSLINKING IN 7.5 mol. dm^{-3} NITRIC ACID SOLUTION



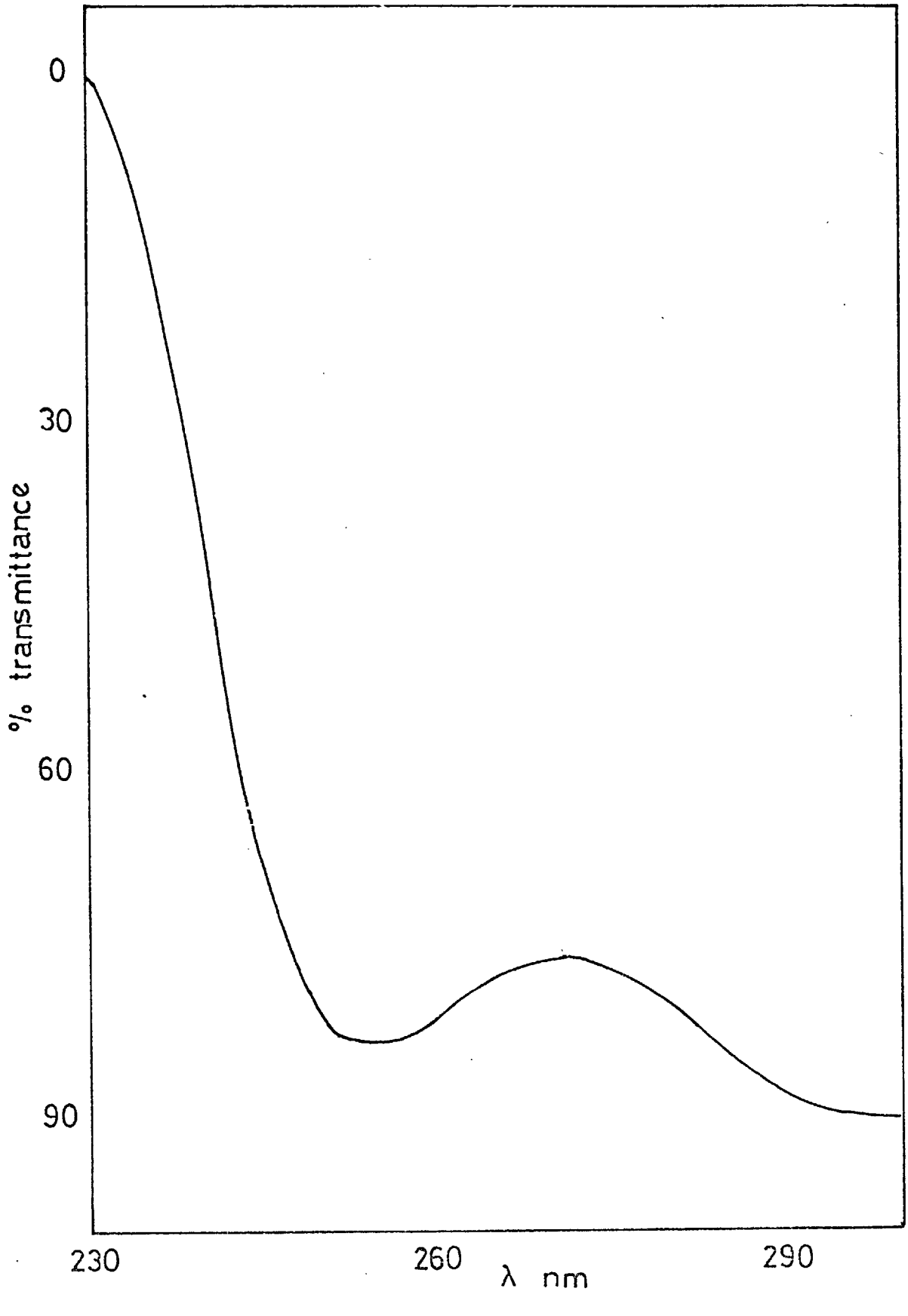
GRAPH 5.3

UPTAKE OF IODIDE (m.mol. g^{-1}) ON TO NITRATE FORM XAX 1284 WITH TIME (days) FROM AQUEOUS SOLUTION



GRAPH 5.4

SPECTRUM OF SOLUTION (% TRANSMITTANCE VERSUS WAVELENGTH (nm),) OF IODIDE IN CONTACT WITH NITRATE FORM IONAC XAX 1284



SUGGESTIONS FOR FURTHER WORK

SECTION SIX

6. SUGGESTION FOR FURTHER WORK

This work has shown that iodine may be removed from aqueous streams by crosslinked polyvinylpyridine. This may be of use in nuclear technology. However, in this work iodine has been isolated from radiation fields and other fission products. Before the results could be applied directly, experimental ~~empirical~~ work in the presence of such contaminants would have to be performed.

Iodine has been shown to be less of a problem in an ion exchange process than in solvent extraction. Again the experimental work isolated iodine and the influence of contaminants is likely to be important.

Finally, it is possible that polyvinylpyridine may be useful for removing iodine from solvents other than water. A preliminary study was made of the possibility of separating iodine from tributyl phosphate (T.B.P.). It was found by spectrophotometry that I_3^- was formed in iodine-T.B.P. systems, indicating a charge transfer reaction:-

$$I_2 + TBP \rightleftharpoons TBP.I_2 \quad (1)$$

$$TBP.I_2 \rightleftharpoons TBP.I^+I^- \quad (2)$$

$$TBP.I^+I^- + I_2 \rightleftharpoons TBP.I^+I_3^- \quad (3)$$

When a series of experiments were carried out batchwise, as before, with a three phase system of polyvinylpyridine, water and T.B.P., it was found that most of the iodine could be transferred to the polyvinylpyridine resins. However, a maximum resin capacity of only 0.08 m mol.g^{-1} was obtained after three weeks contact. It may be possible that iodine can be scrubbed from T.B.P. but it will require large quantities of resin. Further study on the removal of iodine from organic solvents would seem to be worthwhile.

REFERENCES

REFERENCES

1. MELLOR, J.W. "Inorganic and Theoretical Chemistry" Sup. 2 Part 1. Longmans 1956.

2. GUTMANN, V. "Halogen Chemistry" 3 Vols. Academic Press 1967.

3. COTTON, F.A., WILKINSON, S. "Advanced Inorganic Chemistry" p.559 Interscience 1966.

4. LEDERER, C.M. et al. "Table of Isotopes" Wiley 1967.

5. BERNARD, S.R. et al. "Health Physics 9 p.1307 1963

6. HOLLAND, J.Z. ibid. p.1075.

7. PERKINS, R.W. ibid. p.1113.

8. NORWALL, H.J., FLOWERS, R.H. UKAEA Report AERE - C/M - 342.

9. CHAMBERLAIN, A.C. et al. J. Nuc. Energy 17 p.519 1963

10. Van MIDDLESWORTH, L. Health Physics 9 p.1197 1963.

11. MORTER, W.L. ibid. p.1105.

12. SAENGER, E.L. ibid. p.1371.

13. LENGERMANN, F.W., THOMPSON, J.C. (jr) ibid. p.1391.

14. GRAUL, E.H. et al. ibid. p.1411.

15. SAX, N.I. "Dangerous Properties of Industrial Materials" Reinhold, N.Y., 1963.

16. ELKINS, H.B. "Chemistry of Industrial Toxicology" Wiley, New York, 1959.

17. WILSON, B.J. "The Radiochemical Manual", p.255, The Radiochemical Centre, Amersham.

18. DILLON, I.G., BURRIS, L. (Jr) USAEC Report ANL - 5742 July 1957 USAEC Report ANL - 5334 Oct. 1954.

19. CASTLEMAN, A.W., SALZANO, F.J. USAEC Report TID - 7641 p.155 - 68, 1963.

20. BAGNALL, K.W. "Halogen Chemistry", (Ed. Gutmann) Vol.3, p.303, Academic Press, 1967.

21. BROWN, P.G. — Private Discussions, July 1969.

22. RUPP, A.F., — USAEC Report ORNL - 1047, Dec. 1951.

23. DREHER, J. et al. — USAEC Report CN - 3285, 1945.

24. GLENDENIN, L. — USAEC Report CC - 2218 1945.

25. FREED, S. et al. — Memorandum No. 47-9-538 1947. reported in reference 22.

26. LATIMER, G. — "The Oxidation States of the Elements" Prentice-Hall Inc., 1938.

27. MOLES, E., PEREZ-VICTORIA, A. — Bol. Acad. Ciemie Exactons Fis. Ouim. (1938) reported in ref. 22.

28. STOLLER, S.M., RICHARDS, R.B. (Editors) — Reactor Handbook, Vol. II. (Fuel Reprocessing) Interscience, 1961, p.122.

29. RAINEY, R.H. et al. — USAEC Report ORNL - 2591, 1959.

30. MAEK, W.J., REIN, J.E. — USAEC Report IDO - 14481, 1959.

31. LEFORT, M. — USAEC Report AEC - tr - 3175, 1950.

32. ZAITSEVA, N.G., CHUNG, L.W. — Radiokhimiya 2 No. 5, p.614-623, 1960.

33. "Reprocessing of Fuel from present and future Power Reactors" Report: KR - 126, 1967, p.88.

34. ibid. p.102.

35. ibid. p.397.

36. HOLM, C.H. — USAEC Report HW - 20803, 1951.

37. HOLM, C.H. — USAEC Report AECD - 3202, 1951.

38. BLAKE, C.A. (Jr) — USAEC Report ORNL-4212, 1968.

39. CASTLEMAN, A.W., et al. — J. Inorg. Nucl. Chem., 30, p.5-13. 1968.

40. EILAND, H.M., KAHN, M. — J. Phys. Chem, 65, p.1317-1320, 1961.

41. KAHN, M., WAHL, A.C. — J. Chem. Phys. 21, p.1185, 1953.

42. GOOD, M.L., EDWARDS, R.R. — J. Inorg. Nucl. Chem. 2, p.196, 1956.

43. GOOD, M.L., WILLIE, R.G. — J. Am. Chem. Soc. 79, p.1040, 1957.

44. GOOD, M.L. — Reported in Edwards, R.R., USAEC Report ORO - 137, 1955.

45. K TZIN, L.I. — J. Chem. Phys., 21, p.490, 1953.

46. CHIA, T.T. — USAEC Report UCRL - 8311, June, 1958.

47. "Nuclear Fuel Reprocessing Research and Development"; Engineer: 224 p.94-6, 1967.

48. Reactor Fuel Processing: 9, p.69-83, 1963.

49. BARONCELLI, F. et al. — Nucl. Sci. Eng., 17, p.298, 1963.

50. Symposium on "Some Operational Problems of Handling and Processing Enriched Fuels": J. British Nuc. Energy Soc., 4, (4), p.368, 1965.

51. KEELER, R.A. et al. — USAEC Report, ORNL - 2301, 1951

52. DAVIES, W. (Jr) — USAEC Report, ORNL - 2764, 1959.

53. SALMON, L.; LOPEZ-MENCERO, E. — Proceedings of Symposium held at Mol, Belgium, on "Processing of Irradiated Fuels" EURATOM Report ETR-203, translated and republished as USAEC Report ORNL-tr-1901, 1967.

54. JONES, S.S. — USAEC Report KAPL-1758, 1958.

55. KEEN, N.J., ALCOCK, K. — UKAEA Report AERE-C/M-186, 1953.

56. SMITH, S.R. — Nucl. Appl., 5, p.20-3, 1968.

57. CEDERBERG, G.K., MacOUEEN, D.K. — USAEC Report IDO-14566, 1961.

58. MARSHALL, R.O. et al. — J. Dairy Science 51 (5) p.673, 1968.

59. STROUP, W.H. et al. — J. Dairy Science 51 (9) p.1500, 1968.

60. WALKER, J.P. et al. — J. Dairy Science 51 (9) p.1373, 1968.

61. COSSLETT, P., WATTS, R.E. — UKAEA Report AERE - R2881, 1959.

62. — "Health Physics Report" ORNL - 1353, 1952.

63. REIMAN, W. et al. — Anal. Chem. 24 p.1199, 1952.

64. ATTERBERG, R.W. BOYD, G.E. — J. Am. Chem. Soc. 72, p.4805, 1950.

65. KRAUS, K.A., NELSON, F. — 1955 Geneva Conference on the Peaceful Uses of Atomic Energy. 7, p.113.

66. AVERSTON, J. EVEREST, D.A. — Chem. and Ind., p.1239, 1957.

67. ZEIGLER, M. — Angew. Chemie., 71, p.283, 1959.

68. SANSONI, B. — Angew. Chemie., 73, p.493, 1968.

69. VULIKH, A.I. et al. — Zh. Fiz. Khim., 42, p.1184, 1968.

70. KSENZENKO, V.I. et al. — Khim. Prom. Moscow. 45, p.786, 1969.

71. BHAT, T.V. RAO, T.V. — Indin. J. Chem. 1, p.497, 1963.

72. HEGDE, R.S. et al. — J. Pharm. Sci., 57, p.598, 1968.

73. COADY, J.R. — Ph.D. Thesis. University of London, 1968.

74. BROWNING, W.E., BOLTA, C.C. — USAEC Report, ORNL - 2116, 1956.

75. IWAMOTO, K. OISHI, J. — J. Nucl. Science and Tech. (Tokyo) 5, (9), p.437-446, 1968.

76. GREGG, S.J. SING, K.S.W. — "Adsorption, Surface Area and Porosity" Acad. Press, 1967.

77. CLARK, T.J., GIBERSON, R.C. — USAEC Report HW-67793, 1961.

78. WARD, A.F.H. — Proc. Roy. Soc. (London), A.133, p.506, 1931.

79. WEISZ, P.B., PRATER, C.D. — Advs. in Catalysis; 6, p.143, 1954.

80. JURA, G.
POWELL, R.E. J. Chem. Phys. 19, p.251, 1951.

81. VERMEULEN, T. Adv. Chem. Eng. 2, p.147, 1958.

82. TRAPNELL, B.M.W. "Chemisorption": Acad. Press, 1955.

83. BARROW, G.M. "Physical Chemistry": McGraw-Hill, 1966.

84. BRUNAUER, S.
et al. J. Am. Chem. Soc., 60, p.309, 1938.

85. LANGMUIR, I. J. Am. Chem. Soc., 38, p.2221, 1916.

86. HUDSWELL, F.
et al. UKAEA Report AERE-R-3183, 1960.

87. MEINKE, W.W.,
WAHLGREEN, M.A. Nucleonics 15, (9), p.156-158, 1957.

88. MORRIS, J.B.,
RUMRARY, C.H. UKAEA Report AERE-R-4219, 1963.

89. MORRIS, J.B.
et al. UKAEA Report AERE-R-4114, 1962.

90. ADAM, R.E.,
BROWNING, W.E. USAEC Report CF-58-5-59, 1958.

91. McCONNON, D. USAEC Report HW-77126, 1963.

92. "Reactor Chemistry Division - Annual Progress Report for Period ending Jan. 31. 1960" ORNL-2931, p.176-181.

93. IWAI, S. et al. Journ. Atomic Energy Soc. of Japan. 9, (5), p.249-258, 1967.

94. DAVIES, R.J. USAEC Report ORNL-4126, 1967.

95. BARRY D.A. et al. USAEC Report BMI-x-10229 1967.

96. TALBOYS, A.P. (John Hopkins Univ.) "Contamination of Metal Surfaces by I^{131} in Solution: Final Report": NYO-1573, 1951.

97. HARLEY, J.H. et al. Nature 197, p.1230, 1963.

98. HARDER, B.R., SNOWDON, R.G. USAEC Report AERE-R-3537, 1960.

99. WATSON, J.W., PARKINSON, D. Ind. Eng. Chem., 47, p.1053, 1955.

100. KIPLING, J.J. et al. Trans. Faraday Soc., 60, p.401, 1964.

101. DAVIES, G. J. Chem. Soc. 91, p.1666, 1901.

102. FRITH, T.F., WATSON, P. J. Chem. Soc. 123, p.1219, 1923.

103. URBANIC, V., DOMERALL, P.J. J. Phys. Chem., 45, p.1245, 1941.

104. FORSYTH, P.E., et al. J. Chem. Phys., 2 , p.66, 1954.

105. TOPCHIEV, A.V. "Radiolysis of Hydrocarbons": Elsevier p.143, 1964.

106. VOGEL, A.J. "Ouantitative Inorganic Analysis" Longmans, 1964, p.343.

107. SNELL, F.D. et al. "Colorimetric Method of Analysis" Van Nostrand, 1959: Chapter 53, p.621.

108. MEYERSTEIN, D. TRENIN, A. Israel Atomic Energy Authority Report IA-763, 1962.

109. EVANS, P.F. J. Chem. Phys. 23, p.1424, 1955.

110. SCROGGIE, L.E. — USAEC Report ORNL-TM-724, 1963.

111. BLANCHARD, R.L. et al. — J. Am. Water Works Assoc. 51, p.967-980, 1959.

112. COTTINO, F., et al. — Nucl. Activ. Tech. Life Sci., Prod. Symp. Amsterdam, 1967. p.419.

113. LEDDICOTTE, G.W., REYNOLDS, S.A. — USAEC Report ORNL-1443, 1953.

114. WAY, K. HAINES, G. — Canadian Atomic Energy Authority Report, AECD-2138, 1948.

115. PERKINS, R.W. — Proc. U.N. Conf. "Peaceful Uses of Atomic Energy": 2nd. Geneva. 28, p.445-461, 1958.

116. RHODES, B.A. — Anal. Chem. 37, p.995-997, 1965.

117. LOVERIDGE, B.A., GORDON, M.S. — UKAEA Report AERE-R-5406, 1967.

118. DICKINSON, G.W. WHEELER, G.V. — USAEC Report, IDO-14591, 1962.

119. TAYLOR, W.H., WEBB, M.S.W. — UKAEA Report AERE-R-3873, 1961.

120. LEDERER, C.M. et al. "Table of Isotopes": Wiley, 1967 p.272.

121. LEDERER, C.M. et al. ibid.

122. WILSON, B.J. (Ed.) "The Radiochemical Manual" Radiochemical Centre, 1966.

123. FRIEDLANDER, G. et al. "Nuclear and Radiochemistry" Wiley, 1964, p.436.

124. CROUTHEMEL, C.E. 125. et al. USAEC Reports: AECU-237 ISC -33 1949.

126. CROUTHEMEL, C.E. et al. J. Am. Chem. Soc. 71, p.3031.

127. GOOD, M.L. et al. J. Inorg. Nucl. Chem. 6, (1), p.73. 1958.

128. EGOROV, E.V., NOVIKOV, P.D. "Action of Ionising Radiation on ion-exchange Materials". Israel Programme for Scientific Translations. 1967, p.132.

129. VERMEULEN, T, Adv. Chem. Eng., 2, p.147, 1958.

130. VERMEULEN, T. — Ind. Eng. Chem. 45 p.1664, 1953.

131. HELFFERICH, F. — Angew. Chem. Inor. Ed. Engl. 1, p.440, 1962.

132. HIESTER, N.K., VERMEULEN, I. — Chem. Eng. Prog., 48, p.505, 1952.

133. KOLTHOFF, I.M., SANDELL, E.B. — "Textbook of Quantitative Inorganic Analysis" MacMillan 1952, p.591.

134. Ibid. — p.627.

135. TURNER, J.C. — "Sample Preparation for Liquid Scintillation Counting". The Radiochemical Centre, Amersham. Review 6, Oct. 1967.

136. — Rohm and Haas Ltd. Technical Bulletin EX-S-636, Jan. 1969.

137. LEDERER, C.M. et al. — Table of Isotopes. Wiley, 1967. p.561.

138. SIEGBAHN, K. (editor) — α,β, γ -Ray Spectroscopy. Volume One. North Holland Publishing Company, 1968, p.256.

139. JAMES, D.B. COOPER, R.S. — USAEC Report LA-2838, 1965.

140. HELFFERICH, F. "Ion Exchange" McGraw-Hill, 1962, p.5.

141. CRASKE, J.M. Ph.D. Thesis. London University, 1971.

142. PRIME, D. M.Sc. Thesis, London University, 1968.

143. COTTON, F.A.
WILKINSON, G. "Advanced Inorganic Chemistry" Interscience 1966, p.563.

144. ANDREWS, L.J.
KEEFER, R.M. Adv. Inorg. Chem. Radiochem. 3, p.91, 1961.

145. SYKES, P. "A Guidebook to Mechanisms in Organic Chemistry" Longmans, 1965, p.101.

146. COADY, J.R. Ph.D. Thesis. London University, 1968, p.68.

147. MARINSKY, J.A. (editor) "Ion Exchange. A Series of Advances". 1 Chapter 6 (Author GOLDRING, L.S.) Dekker Inc. 1966.

148. AUDRIETH, L.F.,
BIRR, E.J. J.A.C.S., 55, p.668, 1933.

149. BENESI, H.A.,
HILDEBRAND, J.H. J.A.C.S., 72, p.2273, 1950.

150. REID, C., MULLIKEN, R.S. — J.A.C.S., 76, p.3869, 1954.

151. KATZIN, L.I. — J. Chem. Phys., 21, p.490, 1953.

152. NOVIKOV, S.S., et al. — Russ. Chem. Rev., p.671, 1962.

153. BIST, H.D., PERSON, W.B. — J. Phys. Chem., 73, p.482, 1969.

154. MORIGUCHI, I, et al. — Chem. Pharm, Bull. Tokyo, 17, p.2088 1969.

155. DWIVEDI, P.C. — Curr. Sci., 39, p.107, 1970.

156. VALDESCO, J.L. — M.Sc. Thesis, London University, 1970.

157, COADY, J.R. — Ph.D. Thesis, London University, 1968, p.52.

158. HELFFERICH, F. — "Ion Exchange" McGraw-Hill, 1962, p.

159. FROST, A.A., PEARSON, R.G. — "Kinetics and Mechanisms", Wiley, 1961, Chapter 2.

160. LAIDLER, K.J. — "Chemical Kinetics" McGraw-Hill, 1966, Chapter 1.

161. SMITH — Private Communication, Radiochemical Centre. Amersham.

162. HELFFERICH, F. — "Ion Exchange" McGraw-Hill, 1962, Chapter 6, p.250.

163. PETERSON, S. — Anals of the New York Academy of Sciences, 57, Article 3, p.144.

164. APPLEBAUM, S.B. — "Demineralization by Ion Exchange". Academic Press, 1968, Chapter 11, p.297.

165. JAMES, D.B. — USAEC Report LA-3499, 1966.

166. HELFFERICH, F. — "Ion Exchange" McGraw-Hill, 1962. Chapter 5, p.151.

167. ibid. — Chapter 6, p.250.

168. ibid. — Chapter 6, section 6-4 p.286.

169. LAIDLER, K.J. — "Chemical Kinetics", McGraw-Hill, 1965, Chapter 6, p.256.

170. ibid. — Chapter 6, p.260.

171. TOMPKINS, F.C. — Trans. Faraday Soc., 46 p.569, 1950.

172. SLYGIN, A. Acta Physicochim., 3, 791, 1935.
FUMKIN, A.

173. LAIDLER, K.J. "Chemical Kinetics" McGraw-Hill, 1965, Chapter 6, p.265.

APPENDICES

APPENDIX ONE

IODINE-125

APPENDIX ONE

IODINE-125

In addition to the sodium iodide well crystal spectrometry, an energy scan was carried out on a iodine-125 labelled iodate source with a proportional counter (20th Century Electronics Ltd. model PX 130 00/XE, a Xenon-methane filled counter with a thin aluminium window).

The proportional counter consists basically of a gas filled chamber containing an anode and a cathode. The gas is ionised by the incident radiation passing into the chamber. Electrons produced by this ionisation are accelerated towards the collector anode and cause further ionisations. The final output pulse is proportional to the single ionisation event which caused it.

A few drops of iodine-125 labelled aqueous potassium iodate were evaporated on a stainless steel planchette to provide a source for the counter. The output from the counter was fed into a multichannel analyser and a spectrum of channel number (i.e. the energy of the incident radiation) versus countrate was obtained. (Graph A1).

To determine the actual energies of these peaks and those of the sodium iodide crystal peaks (graph 2.8), it was necessary to calibrate both counters with a suitable low energy γ-ray standard source. Americium-241 was proved suitable for this purpose, the energies of its emitted radiations are given in table A.1.

From these values and energy scans performed as before with the Americium on the two different counters (graphs A.2 and A.3), calibration curves could be constructed (graphs A.5 and A.4) to determine the energy of the Iodine-125 radiations that were detected.

The decay of Iodine-125 (Figure 2.1) leads to a whole range of radiations. Electron capture results in the formation of a metastable

state of Tellurium-125. It also causes a cascade of electrons because of the vacancy resulting from the capture. Each electron transition results in the emission of an X-ray of energy the difference between that of the electron levels. Hence, an electron jump from the L shell to the K shell will result in the emission of an X-ray of energy equal to the difference between the two electronic levels. This means that for each electron capture a series of K, L, M etc. X-rays will be emitted.

It is also possible that the X-ray emitted may be used in an internal photoelectric process, in which an electron from the L, M, N etc. shell is emitted with a kinetic energy equal to the X-ray energy minus its own binding energy. These electrons are known as "Auger" electrons. This process will lead to further extranuclear rearrangement resulting in further X-ray emission.

Furthermore, the metastable state of tellurium that is formed, decays to the ground state with a half life of only 1.6 ns. This decay occurs by either γ-emission (7%) or by internal conversion (93%). Internal conversion comes about by an interaction between the nucleus and extranuclear electrons which can lead to the emission of an electron. This in turn then leads to further X-ray emission.

Since the half life of the tellurium metastable state is so short, the two X-ray emissions or the X-ray and γ-ray emission can be considered to be instantaneous. If both radiations enter the sodium iodide detector at the same time there will be only one pulse corresponding to the sum of the two energies.

One further complication is that an iodine escape peak may also occur. The incident radiation may eject an electron from the iodine in the crystal. If the corresponding iodine X-ray is lost from the crystal, a pulse corresponding to the difference in energy between the incident radiation

and the iodine X-ray will occur (138).

Radiations that can hence arise from Iodine-125 decay will be:

(a) A 56 x 10^{-16} J γ-ray.

(b) Tellurium X-rays.

(c) "Sum" peaks occurring from the simultaneous detection of X- and γ-rays or two X-rays.

(d) "Escape" peaks.

It should also be pointed out that "sum peaks" will depend on the geometry of counting, since these peaks will only occur when two or more radiations are detected simultaneously. With 4π counting geometry all "simultaneous" radiations will be detected and recorded as sum peaks. As the geometry is decreased, and since radiations are emitted in random directions, less summation peaks will occur, due to the escape of one of the radiations. The counting geometry of the proportional counter was very low, and hence summation peaks would also be rare. However, the sodium iodide crystal counting geometry was much higher and hence summation peaks would be generally detected.

Energies detected by the counters are summarised in table A.2.

TABLE A.1.

ENERGIES OF THE LOW ENERGY RADIATIONS ARISING FROM AMERICIUM-241 (137)

19.043	22.3	28.5
33.3	42.209	95.388

All expressed in 10^{-16} J.

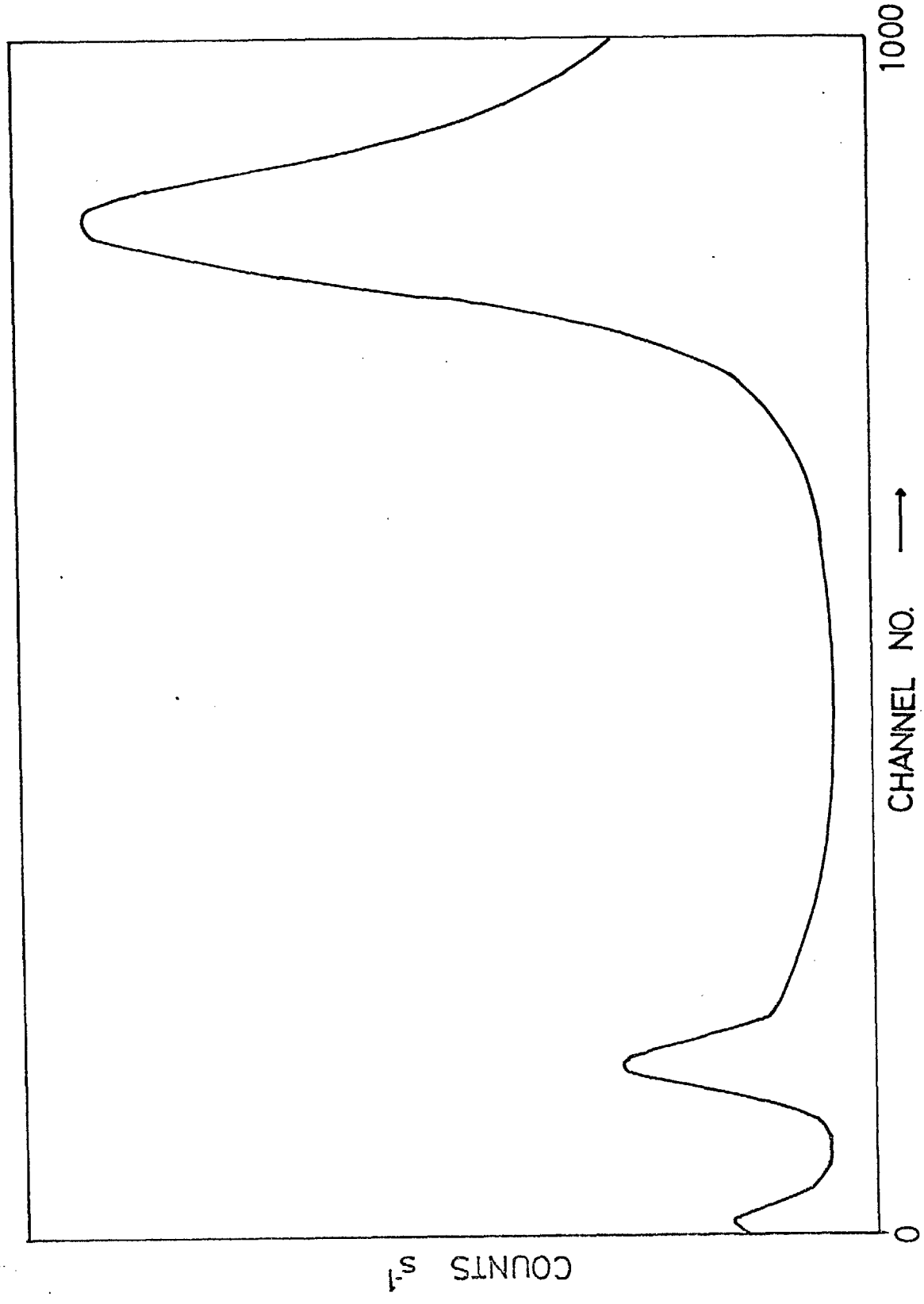
TABLE A.2.

DECAY OF IODINE-125. ENERGY PEAK POSITIONS

COUNTER	PEAK ENERGIES 10^{-16} J	PEAK WIDTHS AT HALF HEIGHT 10^{-16} J
PROPORTIONAL COUNTER	7.4	3.0
	45.7	8.0
SCINTILLATION COUNTER	49.7	18.7
	105.7	24.9

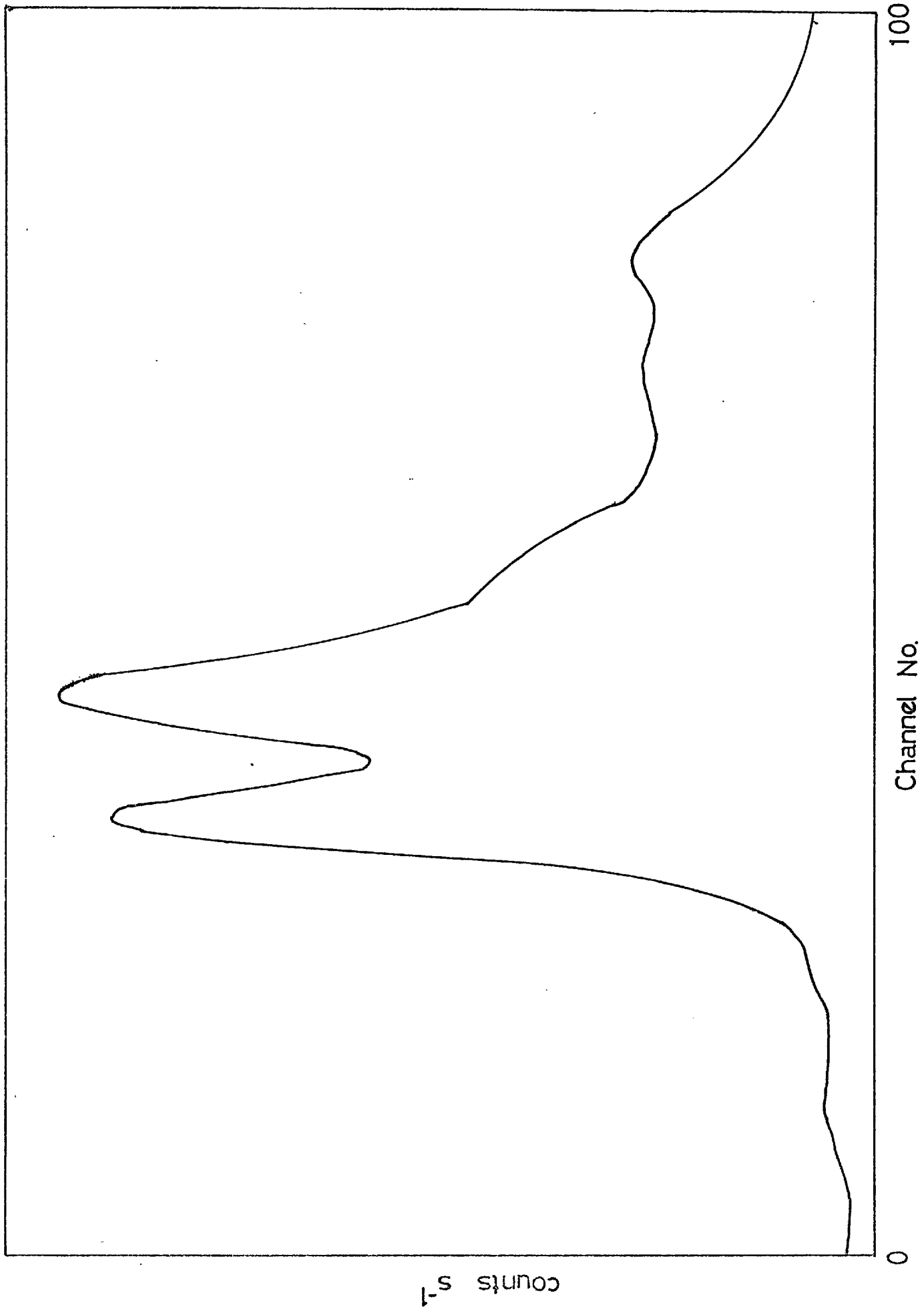
GRAPH A.1

IODINE-125 SPECTRUM COUNTRATE (s^{-1}) VERSUS CHANNEL NUMBER SHOWN BY A PROPORTIONAL COUNTER



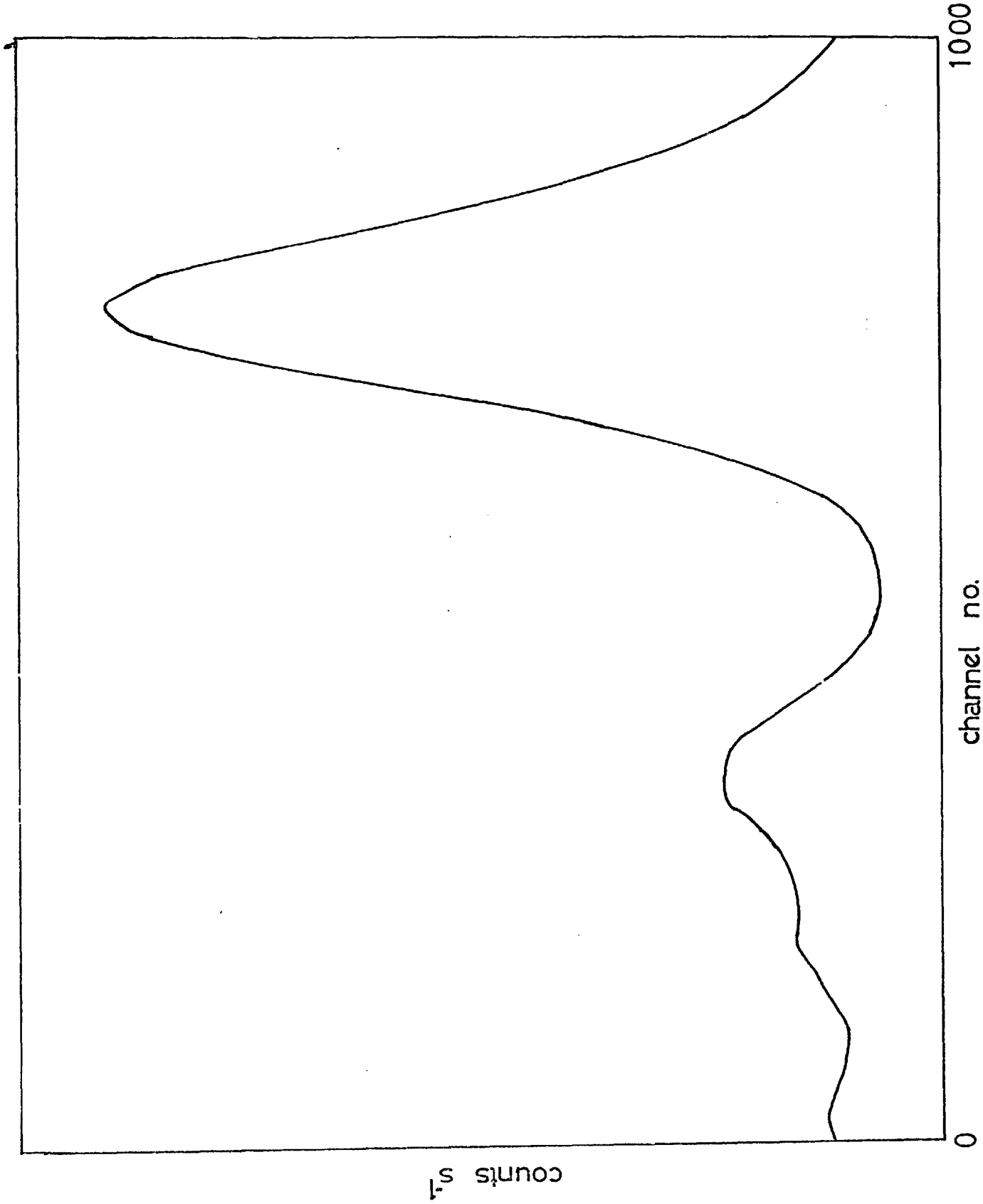
GRAPH A.2

SPECTRUM OF AMERICIUM-241. COUNTRATE (s^{-1}) VERSUS CHANNEL NUMBER SHOWN BY A PROPORTIONAL COUNTER



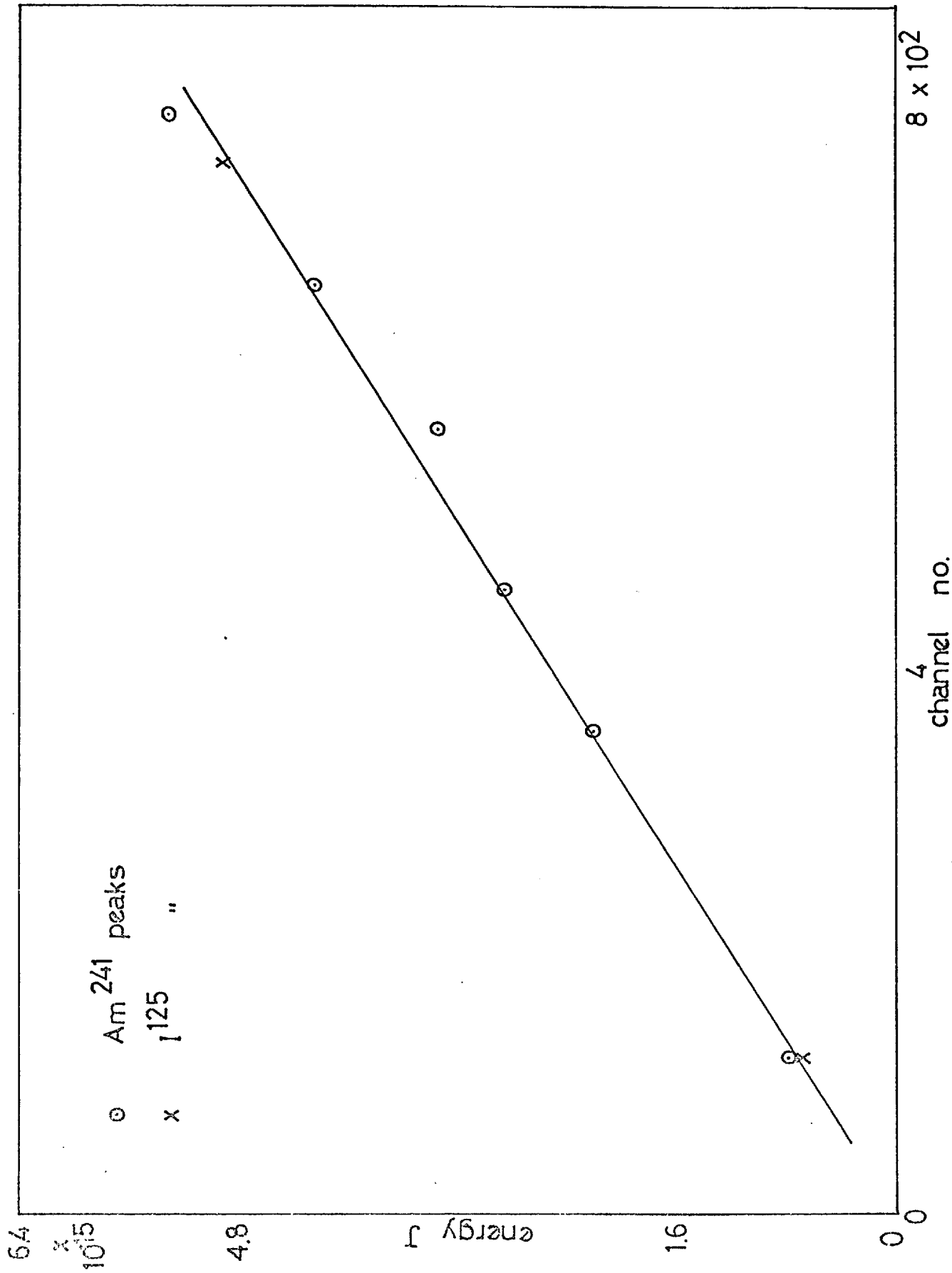
GRAPH A.3

SPECTRUM OF AMERICIUM-241 SHOWN BY A SODIUM IODIDE WELL CRYSTAL

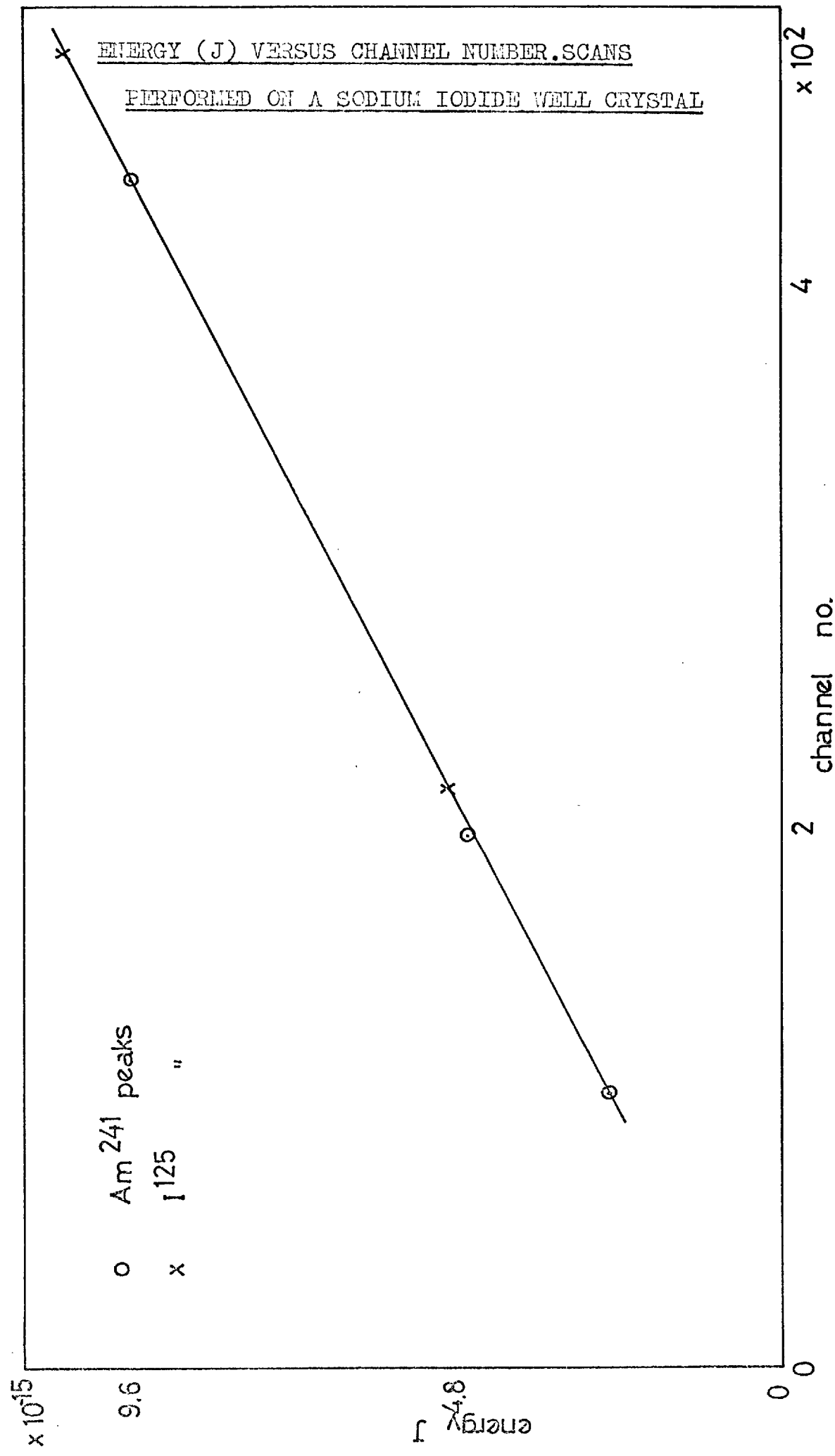


GRAPH A.4

ENERGY (J) VERSUS CHANNEL NUMBER. SCANS PERFORMED ON A PROPORTIONAL COUNTER



GRAPH A.5


ENERGY (J) VERSUS CHANNEL NUMBER.SCANS
PERFORMED ON A SODIUM IODIDE WELL CRYSTAL
o Am 241 peaks
x I 125 "
energy J
x 10^-15
9.6
8.4
0
2
4
x 10^2
channel no.

APPENDIX TWO

RESIN LOADING ACCURACY

APPENDIX TWO

RESIN LOADING ACCURACY

The majority of resin loading results were accurate to within $\pm$ 5%. However, for low loadings or loadings where the solution concentration has changed but little the results were not so accurate. For instance if the solution concentration was measured within 2% where the change was small:

Resin weight = 0.1000 g

Solution concentration change = 0.03 m mol dm^{-3} in 1.00 m mol dm^{-3}

= 0.03 $\pm$ 0.02 m mol dm^{-3}

$\therefore$ Maximum loading = $\frac{0.05}{0.1000} \times \frac{25}{1000}$ = 1.25×10^{-3} m mol g^{-1}

Minimum loading = $\frac{0.01}{0.1000} \times \frac{25}{1000}$ = 0.25×10^{-3} m mol g^{-1}

This reflects a considerable difference, i.e. a 2% error in solution concentration measurement can cause a 250% error in resin loading. Although this is probably a slightly exaggerated example, it does illustrate the difficulty in measurement of resin loadings.