"CHEMICAL EFFECTS OF THE IRRADIATION OF SOLIDS"

THESIS

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CONTENTS

Abstract

This study provides an insight into the sequence of events which take place in crystalline alkali halides following thermal neutron absorption and prompt gamma-ray emission. The object of the work was to clarify certain aspects of "hot atom" chemistry by utilising current concepts of radiation damage theory.

The system chosen for this investigation was potassium iodide, in the form of single crystals. It was postulated that (n,γ) reactions involving the iodine atoms would lead to a series of focused collision sequences in the anion lattice, causing ejection of atomic iodine from the crystal surfaces in certain preferred directions. The problem of detecting these chemically minute amounts of recoiled iodine was solved by having the potassium iodide surfaces labelled with I^{131}, an isotope with a convenient half-life, which would not itself be produced by thermal neutron activation of potassium iodide.

Using the facilities of the Scottish Research Reactor Centre, a variety of experimental techniques, viz., gamma-ray spectrometry, autoradiography, ionic conductivity, etc., has proved that ejection of iodine atoms from the surfaces of single crystals of potassium iodide is preferentially initiated by thermal neutrons, as predicted, and is accompanied by modest lattice damage, in agreement with the proposed mechanism. It has also been shown that the influence of fast neutrons is to cause more extensive lattice damage and consequently fewer collision sequences. In addition, an inverse relationship between crystal surface roughness and yield of ejected iodine has been established.

Various collectors have been developed for the purpose of capturing and localising the energetic iodine atoms recoiled from the crystal surfaces on irradiation; the most successful ones have been palladium/polystyrene, butadiene-acrylonitrile, and activated charcoal/aluminium. The first two types of collector have led to the observation of a remarkable distortion in the gamma-ray spectra of I^{131} recoil atoms when irradiations were conducted at -78°C. A large volume of experimental evidence has been accumulated in elucidating this phenomenon.

When quantitative irradiations and studies of yields were made, it became apparent that the amount of iodine recoiled from the surfaces of the crystals was too high to be accounted for on the basis of mere thermal neutron absorption and prompt gamma-ray emission, causing I^{128} recoil. It is explained, on the basis of theoretical approaches, how this large number of released atoms may be due to a process of multiple ionization, caused by internal conversion and secondary electron

emission following thermal neutron capture. This conclusion was strengthened by taking into account the results of irradiations conducted in a flux of gamma-rays. Should it prove to be correct, it would constitute a most valuable insight into the (n,γ) process in this system.

CHAPTER I

INTRODUCTION

This study is concerned with the mechanism whereby halogen atoms in alkali halides which undergo (n,γ) nuclear transformations can initiate a series of directionally - dependent atomic interactions. The need for such an investigation derives from certain inadequacies in hot atom mechanistic theory. It utilises current concepts of solid state physics radiation damage theory, and thus provides a link between these two disciplines. Such an approach has recently been advocated by Harbottle(1,1).

1.1. Hot Atom Chemistry

Hot atoms are defined as having energies considerably in excess of those required to break chemical bonds. A useful tabulation due to Wolfgang (1,2), which compares hot atom energies with the energies of other processes, is shown in Table 1.

Historically, the first chemical manifestation of hot atoms was the observation by Szilard and Chalmers(1,3), that radioactive iodine could be extracted from ethyl iodide, following neutron irradiation. It was Fermi(1,4) who produced the current explanation for this effect, namely that neutron absorption causes nuclear excitation, which is relieved

TABLE I*

	Particle Physics		Nuclear Physics			Electron Physics			Hot Chemistry		Classical Chemistry		
Type of Bond			Nuclear			Electron-Nuclear			Chemical				
Kinetic Energy (electron volts)	10^{10}	10^{9}	10^{8}	10^{7}	10^{6}	10^{5}	10^{4}	10^{3}	10^{2}	10	1.0	0.1	0.01
Temperature (degrees kelvin)	10^{14}	10^{13}	10^{12}	10^{11}	10^{10}	10^{9}	10^{8}	10^{7}	10^{6}	10^{5}	10^{4}	10^{3}	10^{2}

* From Wolfgang (Ref. 1,2)

by gamma-ray emission and consequent recoil of the isotopic iodine atom with sufficient energy to break its chemical bond to carbon. It is in fact with such (n,γ) phenomena that our investigations are concerned.

The recoil energy, E received by the nucleus in this process can be estimated from the equation

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

where M is the nuclear Mass Number

and E_{γ} is the gamma-ray energy in M.eV.

This, however, is an over-simplification of the position, for the gamma energy is not always emitted as a single photon, but sometimes as a cascade of several gamma-rays for each neutron absorbed. These gamma-rays have a range of energies and will not all be emitted in the same direction, with the result that the atomic recoil momentum will vary widely. The range of energy exhibited by the gamma radiation resulting from thermal neutron capture of I^{127} is shown below(1,5)

Photons/100 Radiative Captures					Highest Energy of γ-Ra
0-1 M.eV.	1-2 M.eV.	3-5 M.eV.	5-7 M.eV.	>9 M.eV.	
30		97	22		6·71

The situation is further complicated by the fact that some of the gamma radiation is undoubtedly internally converted. This may be accompanied by Auger electron emission, thereby inducing a positive charge on the iodine atom, causing it to "explode" from the molecule with considerable momentum.

We shall, for the present, utilise the value of 150 eV., due to Willard(1,6) as the maximum iodine recoil energy following thermal neutron capture, and consider this later in the light of subsequent observations.

It is now well established that radioisotopes produced as a result of thermal neutron irradiation of a compound in dilute solution or in the gas phase are usually obtained in a new chemical form, whereas when pure liquids or solids are irradiated, an appreciable fraction of the total activity is found in the parent compound; this fraction can be expressed as percentage "retention" (e.g. see [1,7]). It would seem that an ordered atomic or ionic lattice can deal with the sudden release of energy at a point within its structure, so as to reduce considerably the amount of expected radiation damage; it is this "self-healing" ability with which we are concerned.

There have been many attempts to explain this phenomenon. Thus Libby(1,8) considered hot atom collisional deactivation processes as a series of hard sphere interactions which degraded the recoiling species to energies of the order of a few electron volts. The "liquid cage" model was then invoked to explain subsequent recombination with the parent molecule.

The situation was further complicated by the observations of Williams (1,9) that retention in crystals could be increased by prolonged neutron irradiation; this phenomenon is known as "pile annealing". Similarly, Maddock(1,10) has observed a thermal annealing process by which the retention in potassium chromate can be improved by heating after neutron irradiation.

In an attempt to incorporate these observations into a general theory of hot atom interactions, Harbottle and Sutin(1,11) invoked a model based on the displacement spike theory of radiation damage(1,12). They considered the energy of the recoil atom to be dissipated in a small region of the crystal which would therefore show a sharp rise in temperature for a period of the order of 10^{-11} sec., during which time chemical interactions could occur. These reactions would not, however, be able to go to completion, due to "quenching" of this "hot zone", but could subsequently do so under the influence of heat (post-irradiation annealing). Similarly, the phenomenon of pile-annealing was explained by assuming that interactions of ionizing radiation with the crystal would give rise to "Thermal Spikes" (e.g. see[1,13]) which, on being generated sufficiently closely to a recoil atom, would endow it with sufficient activation energy to anneal.

One of the main difficulties in the development of valid hot atom theories is, as discussed by Harbottle,(1,1) that they have been based on post-irradiation examinations which usually involve dissolution of the solid. This causes destruction of all sorts of unknown crystal-stable fragments through interactions with the solvent or with each other, and renders any subsequent interpretation open to grave doubt. We have sought to avoid this by maintaining our specimens in their original crystalline form, and using recoil yields, ionic conductivity measurements, etc. to investigate the extent of radiation damage.

1.2. Radiation Damage in Crystals

The classical approaches to this topic(1,14;1,15) considered the interaction of a primary particle and a lattice atom as being described by a two-body collision process, which transferred energy to the lattice atom (referred to henceforth as the 'primary').

If the energy of the latter, Ep, was considerably greater than the energy necessary to displace it from its lattice position, Ed, then it could behave like a projectile and cause further displacements, producing secondary, tertiary, etc. species in a displacement cascade. This would continue until the energy of every particle was insufficient to transfer Ed in subsequent collisions. In this model, the number of displacements arising from each primary event is a function of the energy of the latter, and may be denoted by ν(Ep). Provided that Ep is much greater than Ed, then

$$\nu(Ep) = Ep/2Ed$$ (1,15)

It was found, however, that the density of defects predicted by this theory were greater than those actually observed by factors of from 3 to 10(1,16). The principal reason for this was the assumption of isolated two-body collisions involving randomly-arranged atoms of the solid - that is, a neglect of its ordered atomic nature, and thus of its potential ability to impose restrictions on the extent of radiation-induced displacements.

The first experimental indication of the influence of the crystal lattice arose(1,17) from an originally diverse field of study, viz., cathode sputtering; it had been noted relatively recently that sputtering of atoms from single crystal cathode surfaces occurs in certain preferred crystallographic directions. Wehner(1,18) was the first to study this systematically by bombarding tungsten and silver monocrystalline targets with low energy (125-250 eV.) Hg^+ ions. He observed that atoms were ejected preferentially along the close-packed directions (e.g. the <110> direction in the case of face-centred cubic structure). Thompson(1,19) proved that this was indeed a bulk effect rather than a surface phenomenon by observing preferred ejection from a thin gold crystal on irradiation with a high energy (0.3 M.eV.) proton beam. (Rutherford scattering recoils from the surface would have produced a uniform distribution of recoiled material over the collector).

The theoretical treatment of the extent to which the ordered atomic lattice could influence momentum transfer began when Silsbee(1,20), showed that an energetic primary recoil species could have its momentum focused along certain close-packed lattice directions for trajectories within a certain solid angle. This results in energy being efficiently removed from the initial point of impact in a focused collision sequence, so that energy transfers greater than Ed may be absorbed without the production of additional displacements. This effect could thus account for the discrepancy between the simple theory and experimental observations, particularly in the case of close-packed structures, where the agreement was poorest. It is thus connected with the previously-described "self-healing" property exhibited by crystalline materials on irradiation.

The focusing effect is not important for very energetic species, since they have very large mean free paths within the lattice, and therefore little chance of being influenced by it; it becomes important only when the mean free path is of the same order as the interatomic lattice spacing. There is thus a Focusing Energy, Ef, below which focused collisio sequences should be possible in a particular system; by the same reasoning, they should be more likely to occur along its most close-packed crystalline directions.

The geometrical requirement for Silsbee focusing is shown in Fig. 1,1 where the full line circles represent atoms of diameter D in a close-packed row, separated from one another by distance S. Suppose that the first atom in the row receives an impact which causes it to leave its lattice position at angle θ_1 to the line of centres. When it has reached the positio shown by the first dotted circle, it collides with the second atom, causing it to recoil, at an angle θ_2,

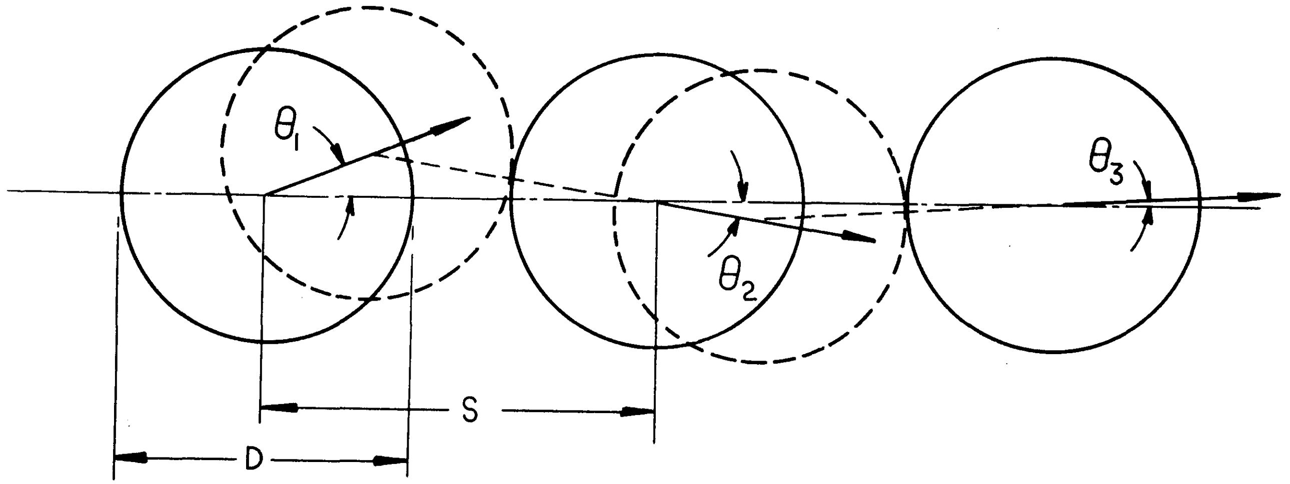


FIG. 1,1

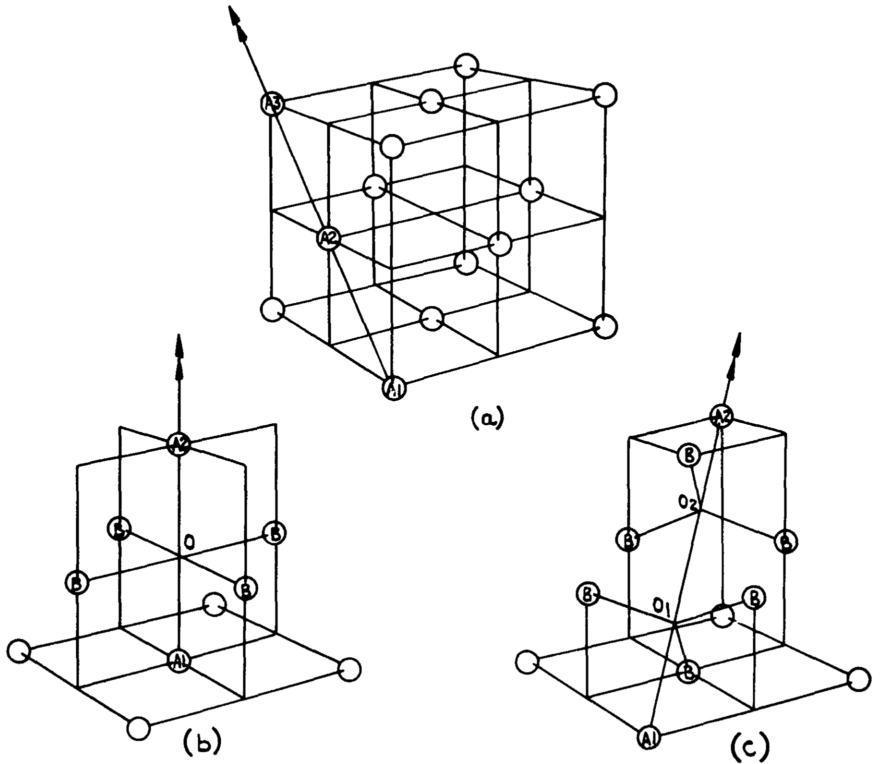
to the position shown by the second dotted circle, colliding with the third atom, and causing it to move off at an angle θ_3. Thus, provided that θ_1 is not too large, each subsequent recoil angle becomes smaller, and momentum is propagated along the row. By this mechanism, the radiation damage is reduced to a minimum, since each atom returns to its original lattice position, unless the collision sequence intersects a surface, when the last atom may then be ejected, provided that it has sufficient energy to overcome the surface binding energy. It may readily be shown that the geometrical requirement for such a momentum transfer is that

$$D/S > 0.5$$

Thus if the separation S is greater than 2D, each successive angle would increase, causing the sequence to rapidly de-focus.

However, it has been shown by Nelson and Thompson(1,21) that it is possible for momentum to be removed from a lattice point even when the above geometrical requirement is not satisfied, by a process of assisted focusing. Fig. 1,2(1,21) shows a face-centred cubic structure, illustrating their findings:

(a) A focused collision sequence in the <110> direction. This transfers energy only, and is sometimes called a focuson.



(a) (b) (c)

FIG. 1,2*

(a) A $\langle 110\rangle$ FOCUSED ENERGY PACKET; (b) a $\langle 100\rangle$, AND (c) a $\langle 111\rangle$ FOCUSED REPLACEMENT SEQUENCE.

* from NELSON and THOMPSON (REF. 1,21)

(b) Atom A_1 passes, in the <110> direction, through a ring of four B atoms, and makes a head-on collision with A_2. In so doing, it suffers four glancing collisions with the B atoms, which assist the focusing in a manner somewhat similar to the action exerted by a converging lens on a beam of light. By the time A_1 collides with A_2, however, it has travelled too far to return to its original lattice position, and so replaces A_2. This is therefore called a focused replacement sequence.

(c) Shows a focused replacement sequence in the <111> direction, assisted by two sets of three B atoms.

Another mechanism of long range transportation of matter is channeling(1,22). By this process, a primary recoil may travel relatively large distances down open channels in the lattice bordered by close-packed rows, in such a way that its interaction with the lattice will be small. This, however, is important only for primaries of high energy.

The original postulates of Silsbee on the importance of the crystal lattice in influencing radiation damage events have been amply verified by sputtering experiments like the significant ones referred to above. They have in addition been confirmed by the relatively recent technique of computer simulation of radiation damage, in which the computer follows the progress of an energetic recoil species as it interacts with others which were originally at rest. This technique has been applied to metals by Vineyard(1,23) and recently, to ionic crystals by Chadderton(1,24). Figure 1,3(1,25) shows a focuson transmitted along the line AE and a focused replacement sequence in which A replaces B, which replaces C, which in turn is ejected into an interstitial position at D.

1.3 The System Under Study

We chose to study (n, γ) reactions in potassium iodide as the medium for generation of focused collision sequences. The geometrical requirement for Silsbee focusing along the <110> direction of the iodide lattice is amply verified, as shown in Table 2.

Plate 1,1 shows a model of the face-centred cubic structure of potassium iodide with the (100) faces exposed, and the close-packed <110> directions clearly visible.

The surfaces of these crystals were labelled with I^{131} by an isotopic exchange reaction so that any surface ejection of atomic iodine could be confirmed by making use of the sensitivity of detection of radioactive species. In this connection, it may

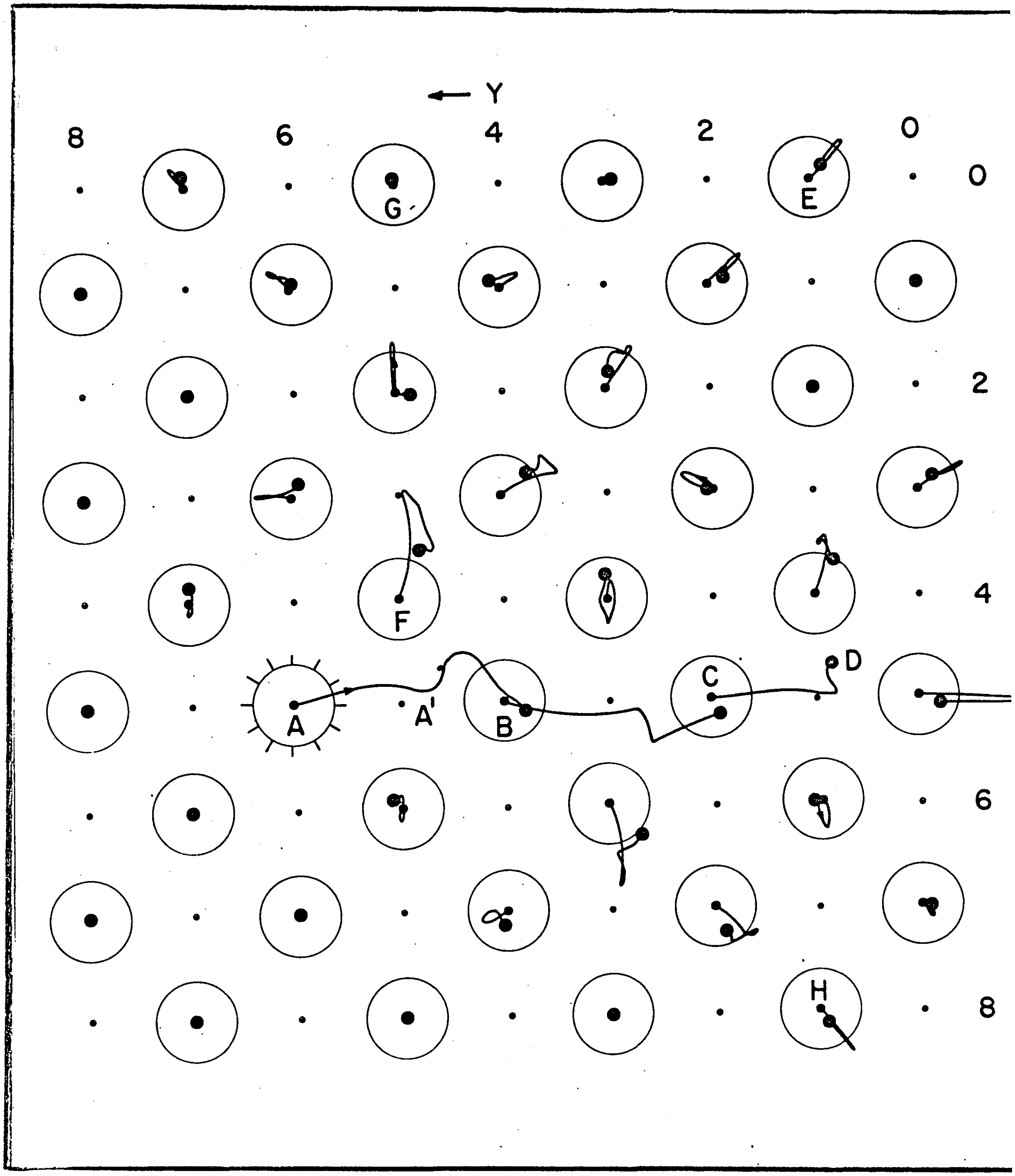


FIG. 1,3

TABLE 2

Substance	Crystal Structure	Ionic or Atomic Diameter (D) (Å)	Interionic or Interatomic Distance (S) (Å)	Ratio of D/S
Potassium Iodide	Face-Centred Cubic	4·336 (I) 2·688 (K)	4·986 (I) 4·986 (K)	0·87 (I) 0·54 (K)
Gold	Face-Centred Cubic	2·88	2·878	1·00
Copper	Face-Centred Cubic	1·92	2·551	0·75
Aluminium	Face-Centred Cubic	1·00	2·859	0·35

N.B. Aluminium is included as an example of a substance which does not exhibit extended focused collision sequences, due to its open structure.

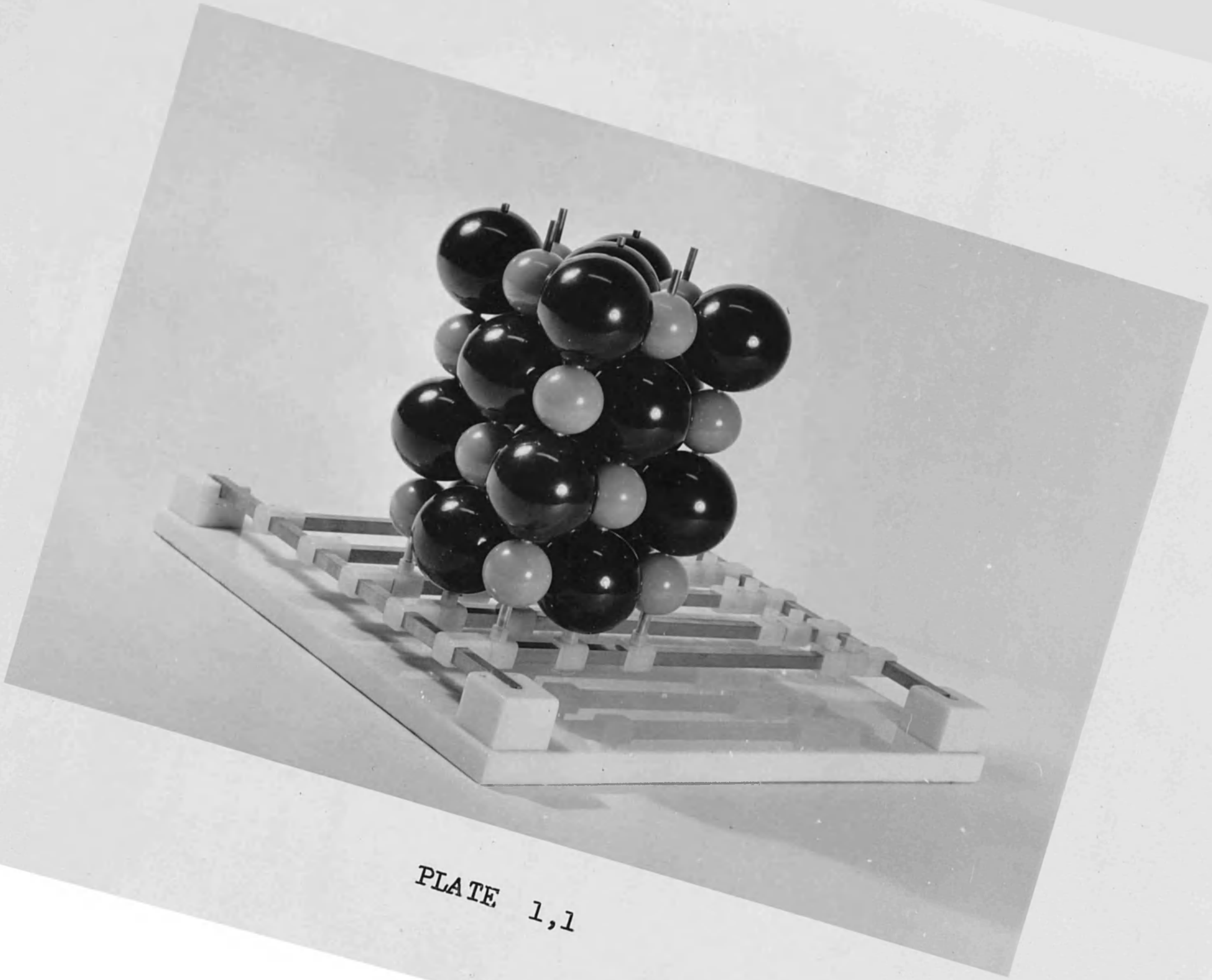


PLATE 1,1

be noted that it is necessary to label with a nuclide which cannot be generated on neutron irradiation, so as to distinguish recoiled species from nuclides produced by (n,γ) events.

From the previous discussion it will be apparent that focused collision sequences could be seriously disrupted by the presence of structural defects in the crystals; care must therefore be taken to ensure that they are well annealed. In addition, the presence of ions of different mass in substitutional positions will seriously disrupt the sequences, for the maximum fraction of energy which can be transferred in a head-on collision is given by the expression

$$4M_1M_2/(M_1+M_2)^2$$

where M_1 and M_2 are the masses of the colliding species. Thus, the crystals should be very pure. For the same reason, it is impossible to obtain extended collision sequences via alternate iodine-potassium interactions.

Finally, it should be noted that the technique of producing atomic displacements by the recoil following an (n,γ) reaction was proposed in 1959 by Schweinler(1,26) for germanium and silicon, and applied to other elements of large thermal neutron cross-section by Walker,(1,27) who calculated the ratio of capture recoil displacements to fast neutron-induced displacements for many elements, assuming the thermal flux to be ten times the fast neutron flux. He found that those elements for which the ratio was greater than unity were Cd, Co, Dy, Eu, Gd, Hg, Ir, Rh and Sm. However, these authors neglected the possibility of focused collision sequences. Thus, in our system, although iodine has a much smaller thermal neutron cross-section (6.7 barns) than any of the above elements, and although the ratio of thermal to fast neutrons in the region of the Reactor where many of our irradiations were conducted is only of the order of 5:1, focused collision sequences generated by (n,γ) processes are so likely that the thermal neutron flux should be all important. This we have found to be the case.

CHAPTER 2

EXPERIMENTAL TECHNIQUE

2.1. The Scottish Research Reactor Centre(2,1)

This is of 100 K.W. maximum power, and was designed by the Advanced Technology Laboratories Division of the American Standard Company. An overall view of the reactor is shown in Plate 2,1. with its principal features displayed on Plate 2,2. It is water-cooled and moderated, with graphite acting as a reflector and, to some extent, as a moderator. There are twelve fuel elements, each consisting of thirteen plates containing 22 g. U-235 in the form of 90% enriched uranium dioxide pellets in an aluminium matrix clad in pure aluminium. These twelve fuel elements are arranged in two parallel rectangular tanks 18 inches apart, contained in a 4ft x 4ft x 5ft graphite block. The flux between the fuel tanks is about 10^{12} neutrons $cm^{-2}.sec^{-1}$, at maximum power, and is remarkably uniform over a large volume. The space is penetrated by five vertical holes, one of which has a cross-section of 6in. x 6in.; this is the one mainly used in this work and it is referred to as the Central Vertical Stringer. In this region, there is, in addition to the thermal flux referred to above, a very considerable epithermal and fast neutron flux, since the cadmium ratio is of the order of 5:1; furthermore, the gamma dose rate is approximately

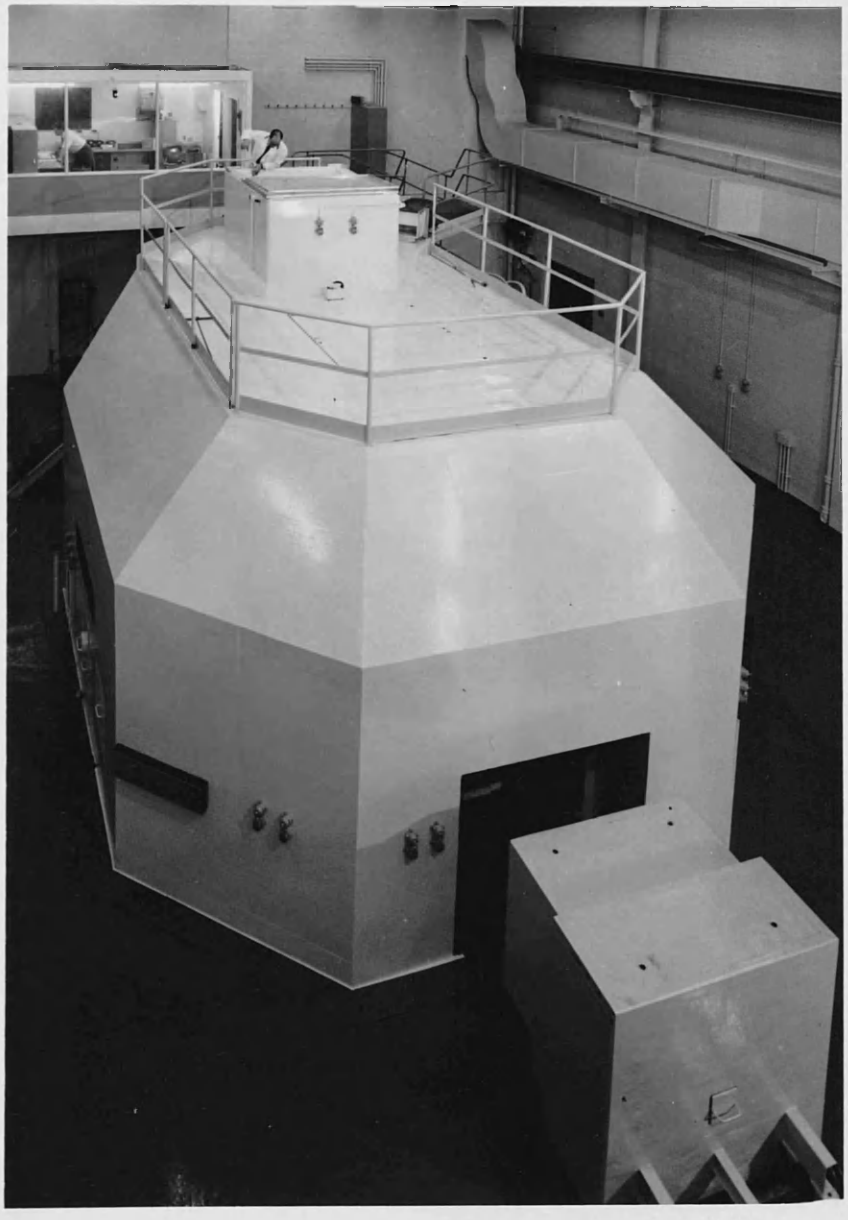


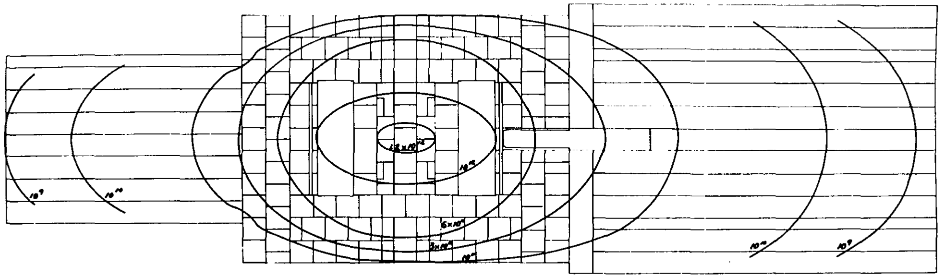
PLATE 2,1

2.5 M. rads/hour. The presence of this mixed flux naturally complicates interpretation of the results, and it will be discussed in greater detail later.

We have also made considerable use of the 4ft x 4ft x 5ft Thermal Column, where the cadmium ratio is of the order of 1,000:1; but, in this region the thermal neutron flux is lower, by about a factor of ten, than that in the Central Vertical Stringer. The Thermal Column has the further disadvantage of being very non-uniform in neutron flux distribution along its length; this latter fact will however be invoked as a contributing factor in a rather curious result to be described later.

The neutron flux distributions in these two regions are summarised in Plate 2,3.

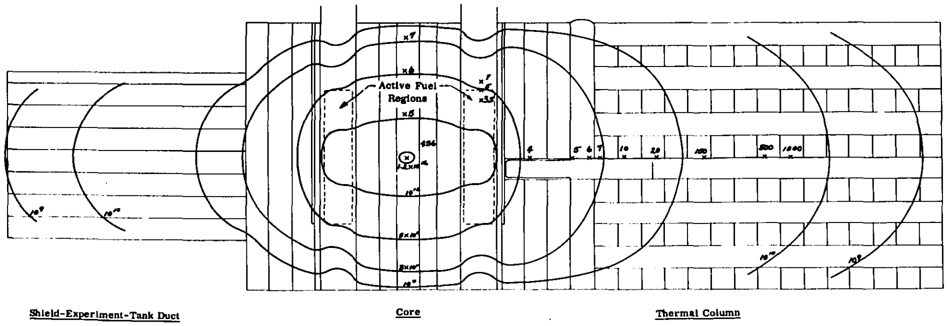
The scintillation counting in this work was performed using as a detector a two and a half inch thallium-doped sodium iodide single crystal, in conjunction with a photomultiplier tube and 512 channel "Laben" pulse height analyser, incorporating an automatic print-out. (Plate 2,4)



HORIZONTAL CENTERPLANE

NOTES: × - POINT WHERE INDICATED VALUE OF CADMIUM RATIO WAS MEASURED.

CONTOUR LINES ARE ISOFLUX LINES. VALUES INDICATED ARE THERMAL-FLUX LEVELS (N/CM^2-SEC) AT A REACTOR POWER LEVEL OF 100 KW.



VERTICAL CENTERPLANE

APPROXIMATE NEUTRON-FLUX DISTRIBUTIONS IN THE UTR

PLATE 2,3

PLATE 2,4

2.2. Preparation of the Crystals

Most of the work to be described utilised single crystals (40 x 5 x 5 m.m.) of pure potassium iodide, cleaved from blocks (40 x 40 x 5 m.m.) supplied by Hilger and Watts Ltd. This material had, according to the manufacturers, been grown by the Kyropolous technique and been annealed for thirty-six hours prior to slow cooling to room temperature.

Spectroscopic examination of these crystals by Johnson, Matthey & Co. Ltd. confirmed their purity, revealing a very low divalent ion impurity content. The analysis figures were:

Element	Parts per Million
Calcium	1
Magnesium	1

Since the cleaved crystals tended to show rather extensive surface dislocations, their surfaces were carefully smoothed, using a Rocksalt PK-01 polishing kit (Research and Industrial Instruments Co., London), which comprises two grades of ground glass plate for smoothing purposes (using AnalaR methanol as lubricant) and a velvet polishing lap with jewellers' rouge for imparting a high polish to the faces. Each crystal was then sealed under vacuum (10^{-4} Torr.) and annealed at 550°C for twenty-four hours, and then cooled to room temperature at a rate of 1 C$^{\circ}$ per minute.

The justification for this latter treatment is, as pointed out by Kun(2,2) that when potassium iodide crystals are produced from the melt by crystal pulling techniques, an important source of defects is thermal stress due to uneven cooling; the cooling takes place partly by axial, and partly by radial heat losses. Owing to the poor thermal conductivity of the alkali halides, a substantial temperature gradient is quickly established between the inner "core" and the outer "skin" of the crystal; since the thermal expansion of potassium iodide is considerable, this differential thermal dilation of the "core" and "skin" will cause stresses, which are relieved by a subsequent heat treatment. The result will be a redistribution of dislocations and probably of point defects. It is thus clear that after the heat treatment, the crystal should be cooled at a rate consistent with its thermal conductivity in order to avoid the reintroduction of stresses. The importance of these considerations in this work shall become more apparent in the subsequent description of the results.

When a crystal of potassium iodide is cleaved as described above, it should have faces of the (100) type, since it has a face-centred cubic structure. This was confirmed by passing a beam of X-rays through a thin representative sample cleaved from one of the crystals, when the very symmetrical X-ray diffraction pattern shown in Plate 2,5 was obtained. However, when the surface layers of one of the crystals which had been subjected to the polishing technique were examined by a Laue back-reflection X-ray technique, they proved to be polycrystalline, due to the extensive cold-working which the crystal had received. When, however, the surfaces were "cleaned" by being immersed in water, then in acetone, they displayed a characteristic back-reflection diffraction effect similar to that shown in Plate 2,5. For this reason, the polishing technique was abandoned, and the crystals were either "cleaned" as described, or merely cleaved immediately before use.

The crystals were prepared for isotopic labelling by being mounted, by means of "Araldite" adhesive, on to a silica rod, placed co-axially in a B24 silica cone. This was done in a dry box, to prevent moisture contamination of the crystals, which were left overnight to allow the adhesive time to harden. Next day, each in turn was inserted in the exchange apparatus shown in Figure 2,1.

2,3 Isotopic Exchange Labelling of the Crystals with Iodine-131

(i) The Exchange Reaction

The surface I^{127} atoms of the single crystals

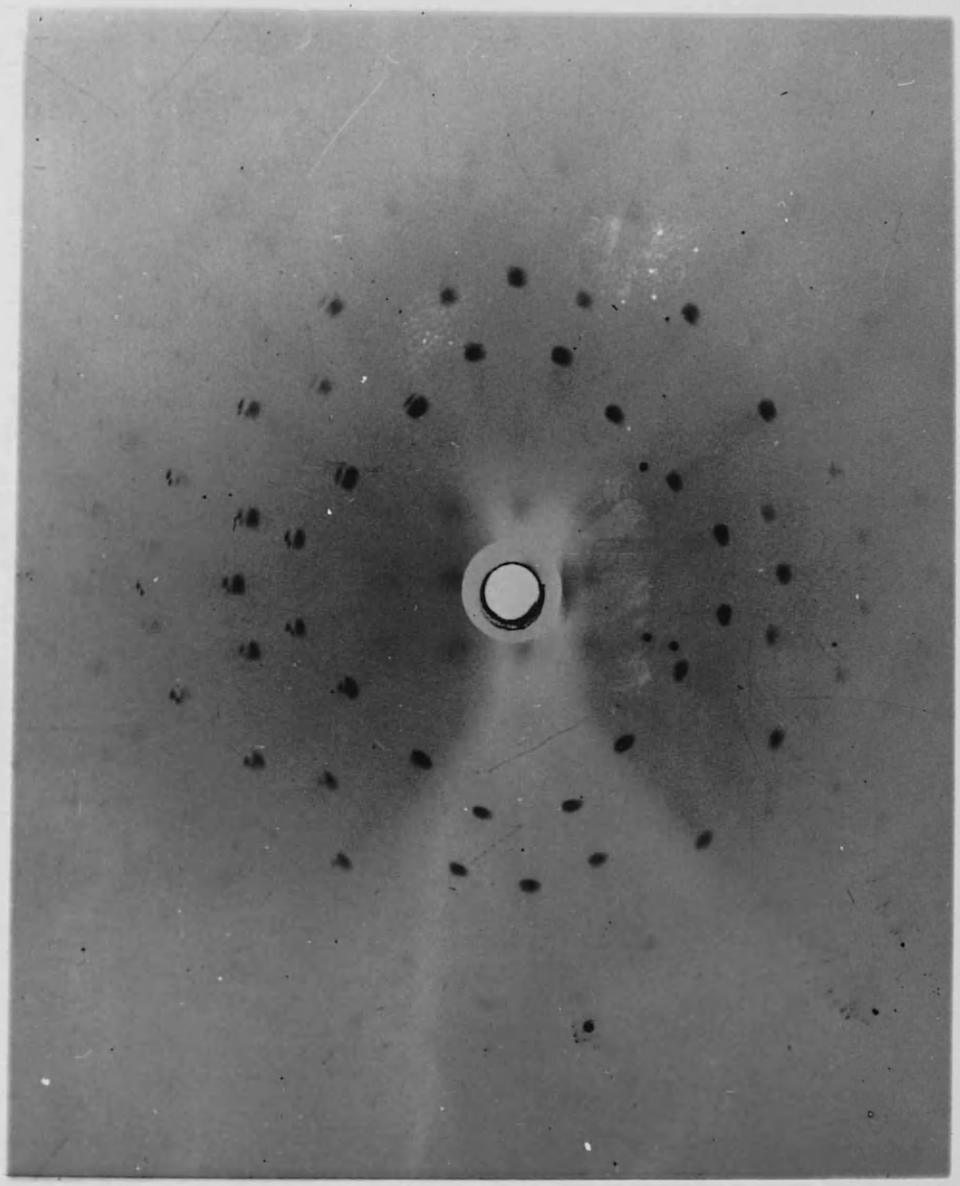


PLATE 2,5

were exchanged in part by I^{131} by means of a gas-solid exchange reaction, for which the I^{131} was generated by thermal decomposition, in vacuo, of palladium iodide;

$$Pd\,I_2 \xrightarrow{350^{\circ}C} Pd + I_2 \text{ ....(I)}$$

(ii) Preparation of Radioactive (I-131) Palladium Iodide

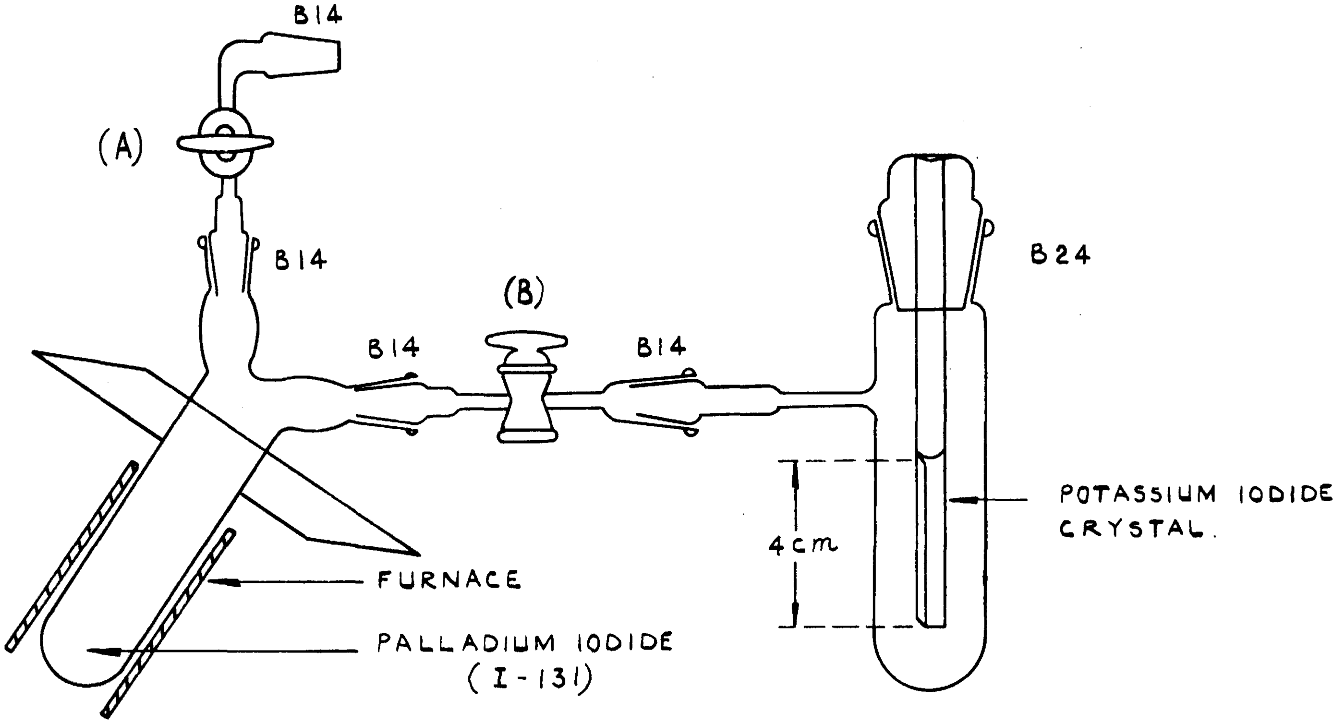
To 2 mc. I^{131} (obtained from the Radiochemical Centre, Amersham, in the form of carrier-free iodide in dilute sodium thiosulphate solution) was added AnalaR potassium iodide (0.45 gm.) as inactive carrier, and, by filtration, palladium chloride (0.32 gm.), dissolved in a few ml. of dilute sodium chloride solution. This produced a black precipitate of palladium iodide, according to the equation

$$2KI + Pd\,Cl_2 \longrightarrow 2\,KCl + Pd\,I_2 \text{ ....(2)}$$

The whole was carefully boiled under reflux in a fume cupboard for a few minutes to coagulate the precipitate, after which it was washed with dilute sodium chloride solution, by being repeatedly boiled and centrifuged, until the washings were colourless (indicating the removal of all excess palladium chloride). The treatment was then repeated, using water instead of sodium chloride solution, until the washings gave no precipitate with dilute silver nitrate solution. Most of the supernatant water was then removed by further centrifugation, and the precipitate finally dried by being connected in vacuo through two U-tubes containing silica gel to a trap filled with liquid nitrogen, and left overnight. (This last step is necessary to prevent the formation of the hydrate of palladium iodide).

The tube containing this labelled palladium iodide was then incorporated in the exchange apparatus shown in Figure 2,1, using KEL-F 90 grease, a chloro-fluoro hydrocarbon grease which resists the attack of iodine vapour. The surface exchange reaction was conducted as follows:-

With taps (A) and (B) open, the system was evacuated to at least 10^{-4} Torr.; then two sliding furnaces were fitted over the tube containing the crystal and that containing the labelled palladium iodide respectively. Their temperatures were raised to approximately 100°C, although their resistances were so chosen as to maintain the tube holding the crystal at a slightly higher temperature than the other tube. This heating in vacuo was continued for at least four hours, at the end of which time the furnace round the crystal was removed. Tap (A) was then closed, and the furnace round the palladium iodide raised in temperature to 360°C to



EXCHANGE APPARATUS.

FIG. 2,1

effect decomposition according to equation (1), whilst, in the meantime, the tube holding the crystal was slowly immersed in liquid nitrogen. When, after fifteen minutes, the furnace was switched off and tap (B) closed, the crystal was completely covered with iodine. The same furnace was then slipped over the tube surrounding the crystal and, with tap (B) still closed, its temperature raised to 90°C. This decomposed the potassium tri-iodide formed on the crystal surface, and allowed the vapour exchange reaction to proceed. After fifteen minutes, tap (B) was once more opened, and, with the tube containing the decomposed palladium iodide now surrounded by liquid nitrogen, the temperature of the furnace was raised to 180°C., and maintained at this value for a further thirty minutes to ensure the removal of all excess free iodine from the surface of the crystal. Finally, tap (B) was closed, and the liquid nitrogen removed, to allow the condensed iodine to be once more re-converted to palladium iodide. In this way, the same batch of radioactive palladium iodide can be used to label several crystals.

The radioactivity on the four longditudinal faces of each crystal was then counted, using an end-window Geiger-Muller tube.

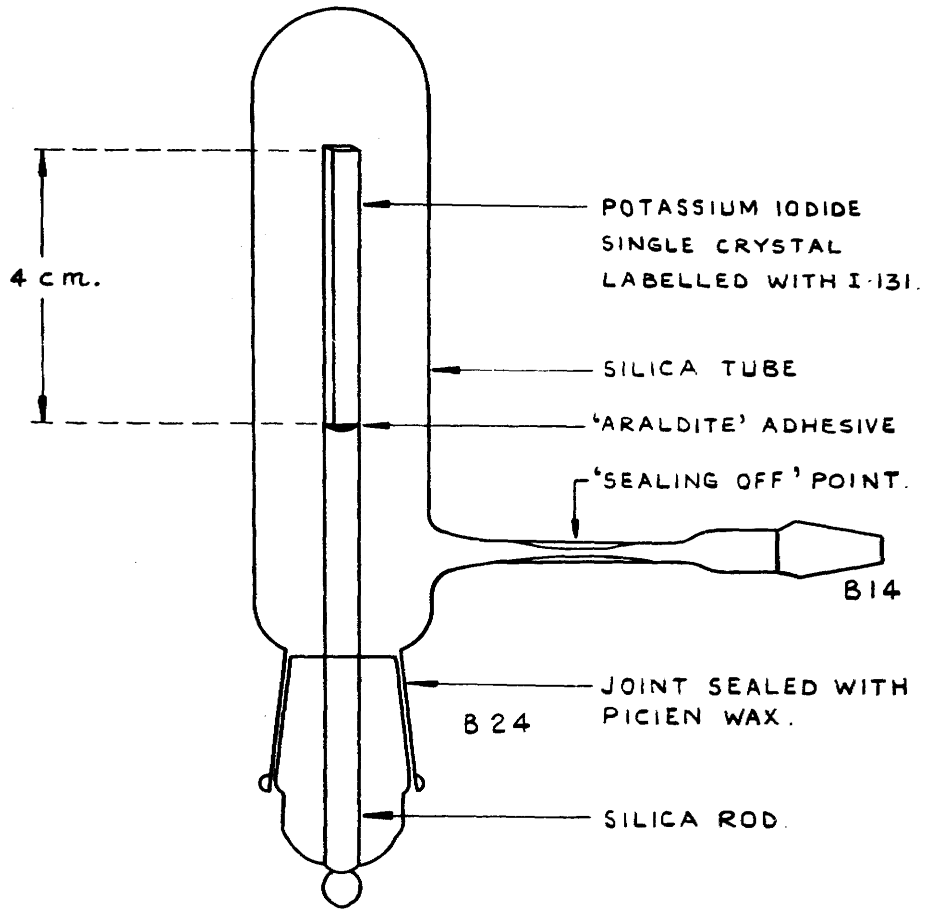
2.4. Early Techniques Employed in Subjecting The Labelled Crystals to Neutron Irradiation

Initially, irradiation of the samples was conducted in the simple apparatus shown in Figure 2,2, which was pumped out overnight at 10^{-4} Torr., sealed off, packed in silica-wool in a Polythene bottle, and irradiated in the Central Vertical Stringer of the Reactor at a flux of approximately 10^{11} neutrons cm^{-2} sec^{-1}. for four hours (at this time, the Reactor could not be run at full power). It was left for three days to allow decay of the induced activity in the silica, after which it was opened by allowing air to enter slowly into the tube through a capillary; the crystal was then removed after softening the Picien wax by gentle heating. The tube was examined, by scintillation counting and autoradiographic exposure, for evidence of I^{131} having been recoiled from the crystal on to its walls.

However, prior to using single crystals, we had performed irradiations on the following crystalline specimens (which were also attached to silica rods by means of "Araldite"):-

(a) Small AnalaR crystals of potassium iodide (Plate 2,6)

(b) Large (approximately 5 m.m.) cubic crystals



METHOD OF MOUNTING POTASSIUM IODIDE CRYSTAL FOR IRRADATION.

FIG. 2,2

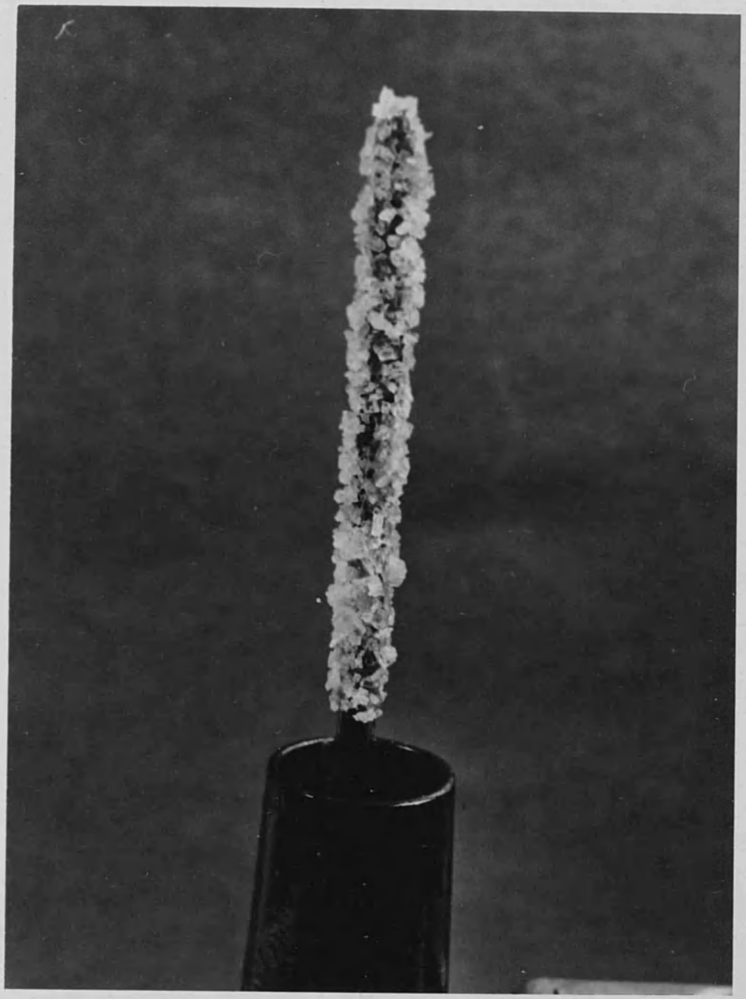


PLATE 2,6

of potassium iodide (Plate 2,7) supplied by Macfarlan Ltd., Edinburgh. These proved to be interesting, because spectroscopic examination by Johnson, Matthey & Co. Ltd. revealed a significant amount of divalent and trivalent impurity ions.

The analysis figures were:

Element	Parts per Million
Calcium	5
Magnesium	1
Aluminium	1

The significance of these figures will become apparent later.

2.5 Ionic Conductivity Measurements on Potassium Iodide

These were recorded by placing the crystal between two platinum electrodes in a nitrogen atmosphere in a silica cell incorporating a thermocouple, and surrounded by a furnace capable of temperatures in excess of 500°C. The actual a.c. conductivity was measured by means of a Wayne Kerr Universal Bridge, B.221. operating at a frequency of 1592 cycles/sec. For a full description of the apparatus and circuit, see McNicol(2,3)

2.6 Autoradiography

(i) Early Techniques

As has been explained earlier, focusing in potassium iodide should occur most readily along the close-packed ⟨110⟩ directions. Thus, if we

PLATE 2,7

irradiate a single I^{131}-labelled crystal of potassium iodide, cleaved so as to expose its (100) faces, it is easy to show that I^{131} should be recoiled on to the inside walls of the surrounding tube in the form of a definite pattern. Such a pattern, which one would expect to find on the inside walls of a 25 m.m. diameter tube, due to preferred ejection along $\langle 110 \rangle$ directions from a single (40 x 5 x 5 m.m.) crystal of potassium iodide, is shown in actual size in Figure 2,3. Random recoils from the crystal surface in such a geometrical arrangement would produce a uniform band of iodine on the inside walls of the tube directly opposite the crystal.

Thus,initially we proposed to detect such a pattern by the technique of autoradiography, in the following manner: after neutron irradiation, the crystal was removed in the usual way, and the silica tube, after having had its gamma-ray spectrum recorded, was set aside for a few days to allow any induced short-lived activity to decay. There was then inserted into the tube three layers of Ilford 'G' X-ray film, this being done, so as to cause as little disturbance as possible, via a narrow bore tube, which was then slowly removed, allowing the X-ray film to expand against the inside walls of

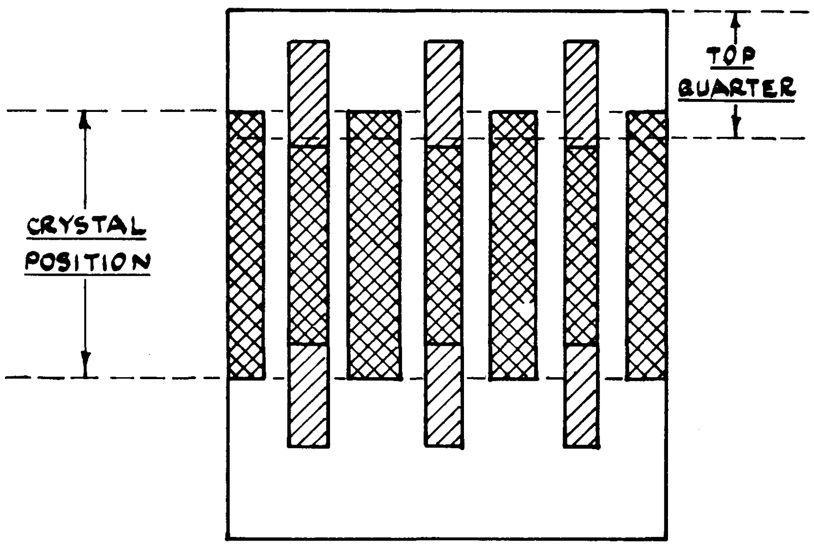


FIG. 2,3

the tube. This technique was not a success, for various reasons to be later elaborated, and was abandoned in favour of that described below.

(ii) Improved Techniques

The above procedure was considerably improved by the incorporation of an iodine-collecting film inside the tube during its irradiation; not only did this favourably displace the equilibrium, but it could be made entirely free from any interfering impurity. After the irradiation, it could be removed and placed in contact with two or more sheets of X-ray film between two sheets of 1/4 inch thick Perspex, which was then wrapped in black paper and stored in a cool place until exposure was complete.

(iii) Calculation of Autoradiographic Exposure Time

In this connection, use was made of the following table, due to Boyd(2,4):

Initial Actvitity and Number of Electrons per sq.cm. Required to Obtain an Optical Density of 0.6 with an Exposure of 15 days

Isotope	Maximum Energy (M.eV.)	Activity (uc./cm^2)	Electrons/cm^2
I-131	0.6	9.8×10^{-4}	2.65×10^{7}

N.B. It should be noted that, strictly speaking, this data applies to Eastman Kodak No Screen X-Ray Film, but this film is so similar to Ilford 'G' that no corrections are required.

Example The activity, A, after a time interval of t days, may be calculated from the basic law of radioactive decay by the expression

$$A = A_o e^{-\lambda t}$$

where λ is the disintegration constant and A_o is the initial activity.

Thus, the total number of disintegrations after a time interval t will be given by

$$Adt = \frac{-A_o}{\lambda} \left[e^{-\lambda t}\right]_o^t$$

$$= \frac{A_o}{\lambda} (1-e^{-\lambda t}) \ldots\ldots\ldots\ldots (i)$$

Suppose the amount of activity on a particular collector film is 3.39×10^{-3} uc/cm^2 (A_2).

From the above table, we may write

$A_1 = 9.8 \times 10^{-4}$ uc/cm^2 and $t_1 = 15$ days.

We may thus calculate the required exposure time (t_2) as follows:

From equation (i),

$$\frac{A_1}{\lambda}\left(1-e^{-\lambda t_1}\right) = \frac{A_2}{\lambda}\left(1-e^{-\lambda t_2}\right)$$

$$\therefore \frac{A_1}{A_2}\left(1-e^{-\lambda t_1}\right) = 1-e^{-\lambda t_2}$$

$$\therefore e^{-\lambda t_2} = 1-\frac{A_1}{A_2}\left(1-e^{-\lambda t_1}\right)$$

$$\therefore t_2 = \frac{-1}{\lambda}\ln\left[1-\frac{A_1}{A_2}\left(1-e^{-\lambda t_1}\right)\right] \quad \ldots\ldots\text{(ii)}$$

Substituting the above values into equation (ii)

$$t_2 = \frac{-8.06}{0.693}\ln\left[1-\frac{9.8\times10^{-4}}{3.4\times10^{-3}}\left(1-\frac{1}{e^{\frac{0.693\times15}{8.06}}}\right)\right]$$

$$= \frac{-8.06}{0.693}\ln\left[1-0.29\left(1-\frac{1}{e^{1.3}}\right)\right]$$

$$= -11.63\ln 0.78$$

$$= 11.63\ln 1.28$$

$$= \underline{2.9\text{ days}}.$$

Thus the exposure time required for any film may be calculated merely by substituting the appropriate figures into equation (ii). The exact estimation of the amount of activity on any particular collector film will be described later in a separate section.

CHAPTER 3

RESULTS

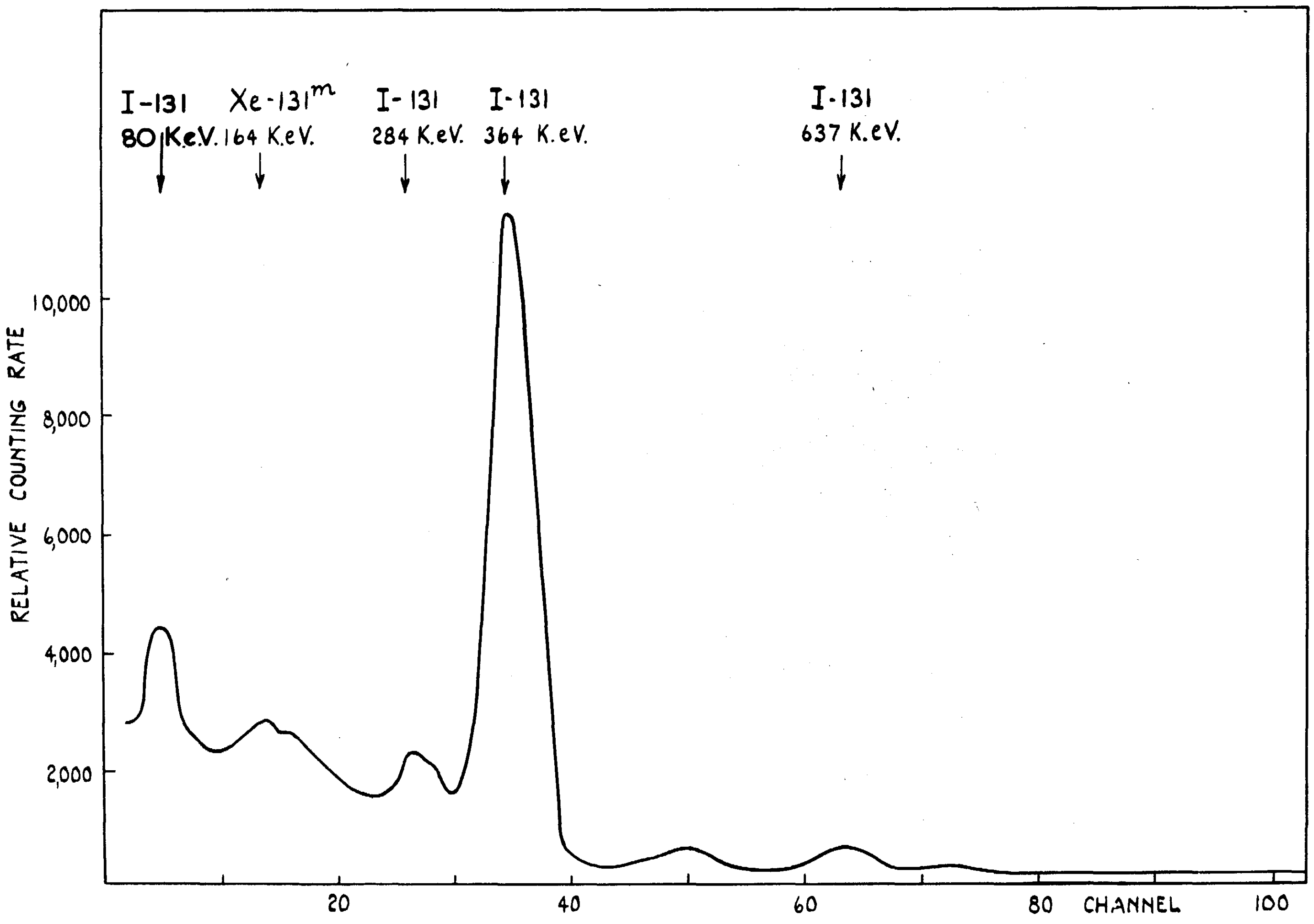
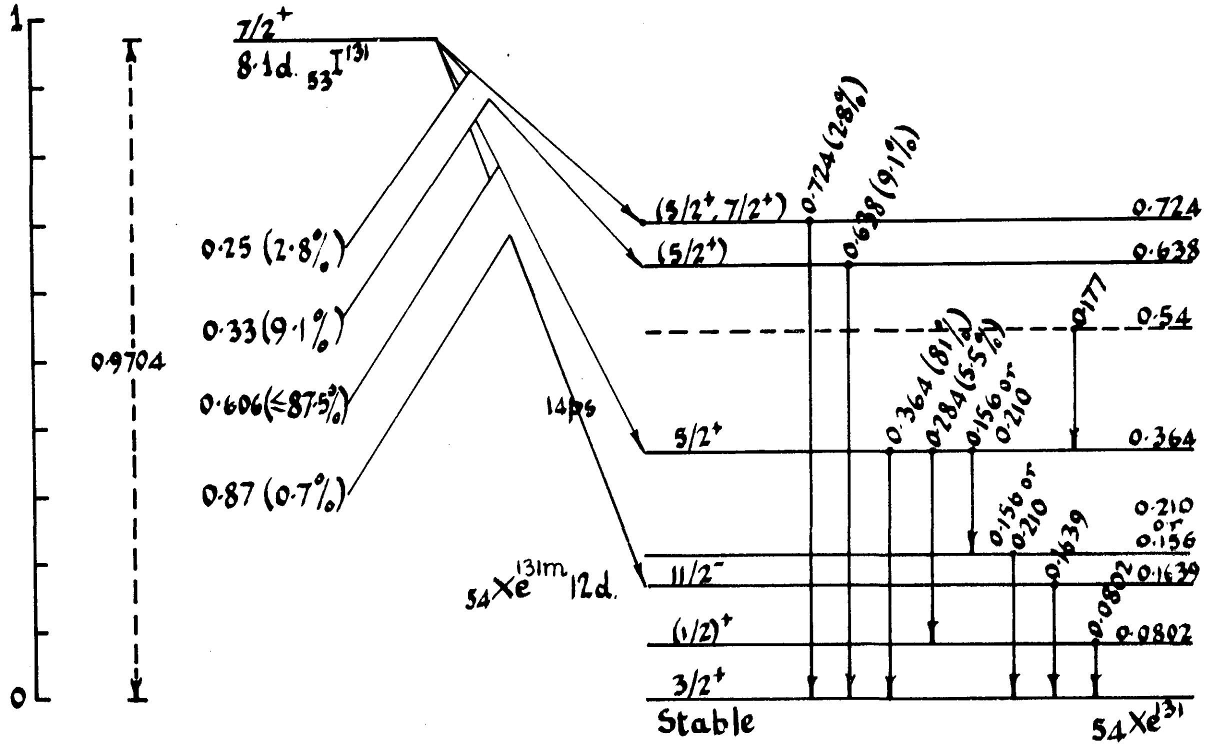

I-131
80 K.e.V.
Xe-131m
164 K.e.V.
I-131
284 K.e.V.
I-131
364 K.e.V.
I-131
637 K.e.V.
RELATIVE COUNTING RATE
10,000
8,000
6,000
4,000
2,000
20
40
60
80
CHANNEL
100

FIG. 3,1



DECAY SCHEME OF IODINE-131

FIG. 3,2

mere mechanical fragmentation of the crystals from the rod on to the inside of the tube. However, the other spectrum, from the large impure potassium iodide crystals, besides showing evidence of I^{131}, also exhibited a number of other peaks. These were identified later as belonging to Cadmium-115, with energies at 490, 520, 260 and 230 k.eV., decaying, with a half-life of 2.2 days, into Indium-115, which exhibits a single peak at 340 k.eV. The nature of this impurity came as a surprise, since no cadmium had been reported in these crystals in the Johnson Matthey & Co. analysis; however, polarographic examination by I.C.I. (Billingham) revealed the presence of cadmium, although in a concentration of only 0.4 parts/million; (they found no trace of cadmium in the AnalaR material). This illustrates the analytical power of activation analysis.

We decided to make use of this observation in order to resolve the difficulty as to whether or not the I^{131} observed on the tubes after the previous irradiations had arrived there as a result of atomic recoils. Two identical crystalline samples of the impure potassium iodide were prepared in exactly the same manner as shown in Plate 2,7, and labelled with I^{131} in the usual way: (their surface count rates were almost identical). One sample (A) was placed in a silica tube, which was evacuated, sealed off, and left aside for three days. The vacuum was then released, the crystals removed, and the tube packed into a Polythene bottle with silica wool for irradiation next day. Meanwhile, the other sample (B) was sealed into another silica tube, which was evacuated, sealed off, and packed into the same bottle. Both samples (one with a crystal, and one without) were then irradiated for 4 hours in a flux of 10^{11} neutrons/cm^2/sec. after which the vacuum in tube (B) was released, and the crystals removed. Both tubes were then washed out with inactive potassium iodide carrier and the iodide in the washings precipitated as cuprous iodide. The gamma-ray spectrum of each precipitate was recorded. The idea behind the experiment was as follows: if the I^{131} has indeed been transferred to the walls by fragmentation, then the gamma-ray spectra from samples (A) and (B) should be of approximately the same shape and magnitude; if, on the other hand, atomic recoils have occurred, then the ratio of the I^{131} peaks, compared to the Cd^{115} peaks, should be greater in sample (B) than in sample (A). The latter result was in fact observed: Figure 3,3 shows the gamma-ray spectrum due to sample (A); Figure 3,4 shows that due to sample (B).

One surprising feature of the spectrum from sample (B) was that the absolute yield of recoiled I^{131} was rather smaller than one would have expected from

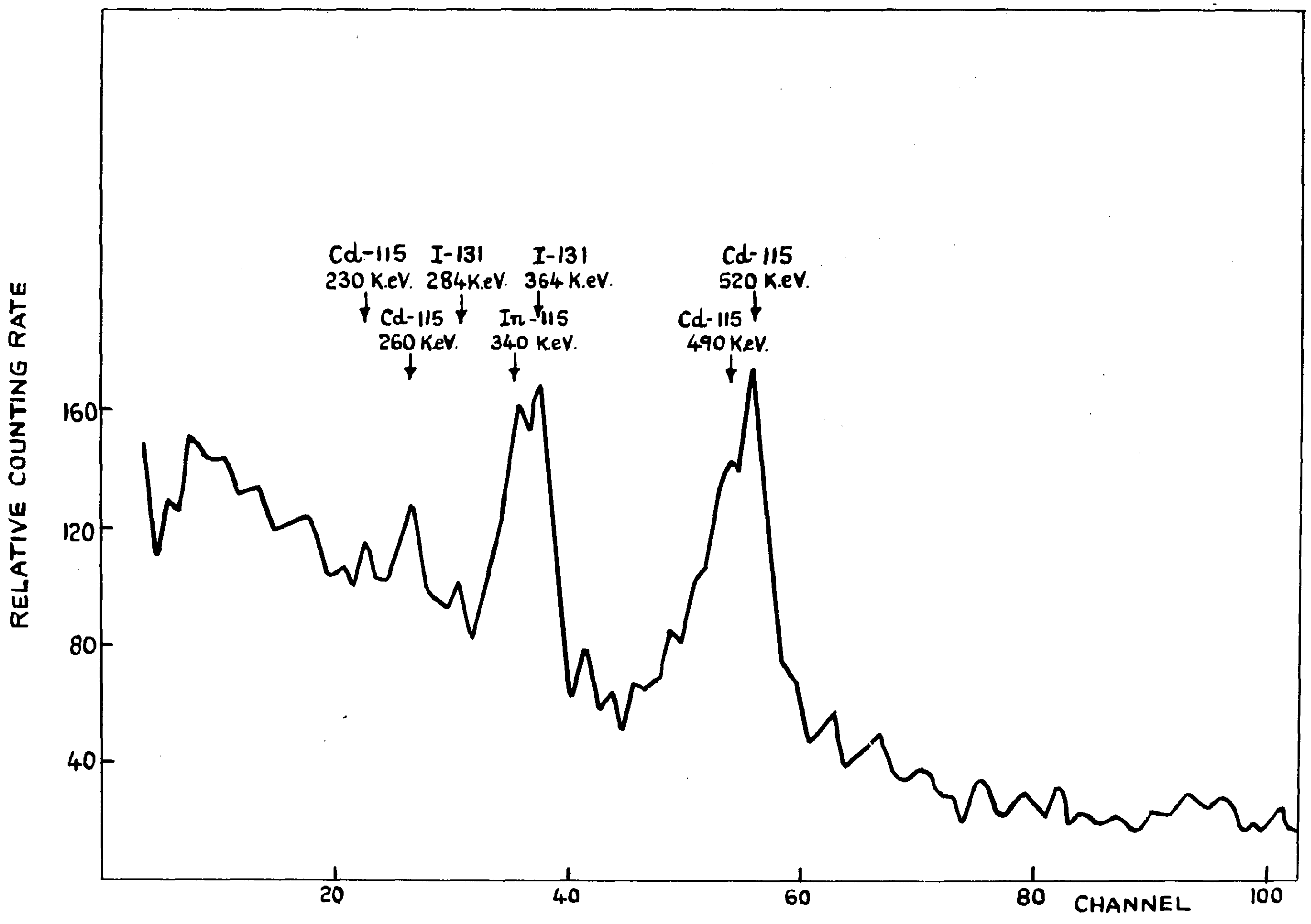

Cd-115
230 K.eV.
I-131
284K.eV.
I-131
364 K.eV.
Cd-115
260 K.eV.
In-115
340 K.eV.
Cd-115
520 K.eV.
Cd-115
490 K.eV.
RELATIVE COUNTING RATE
160
120
80
40
20
40
60
80
CHANNEL
100

FIG. 3,3

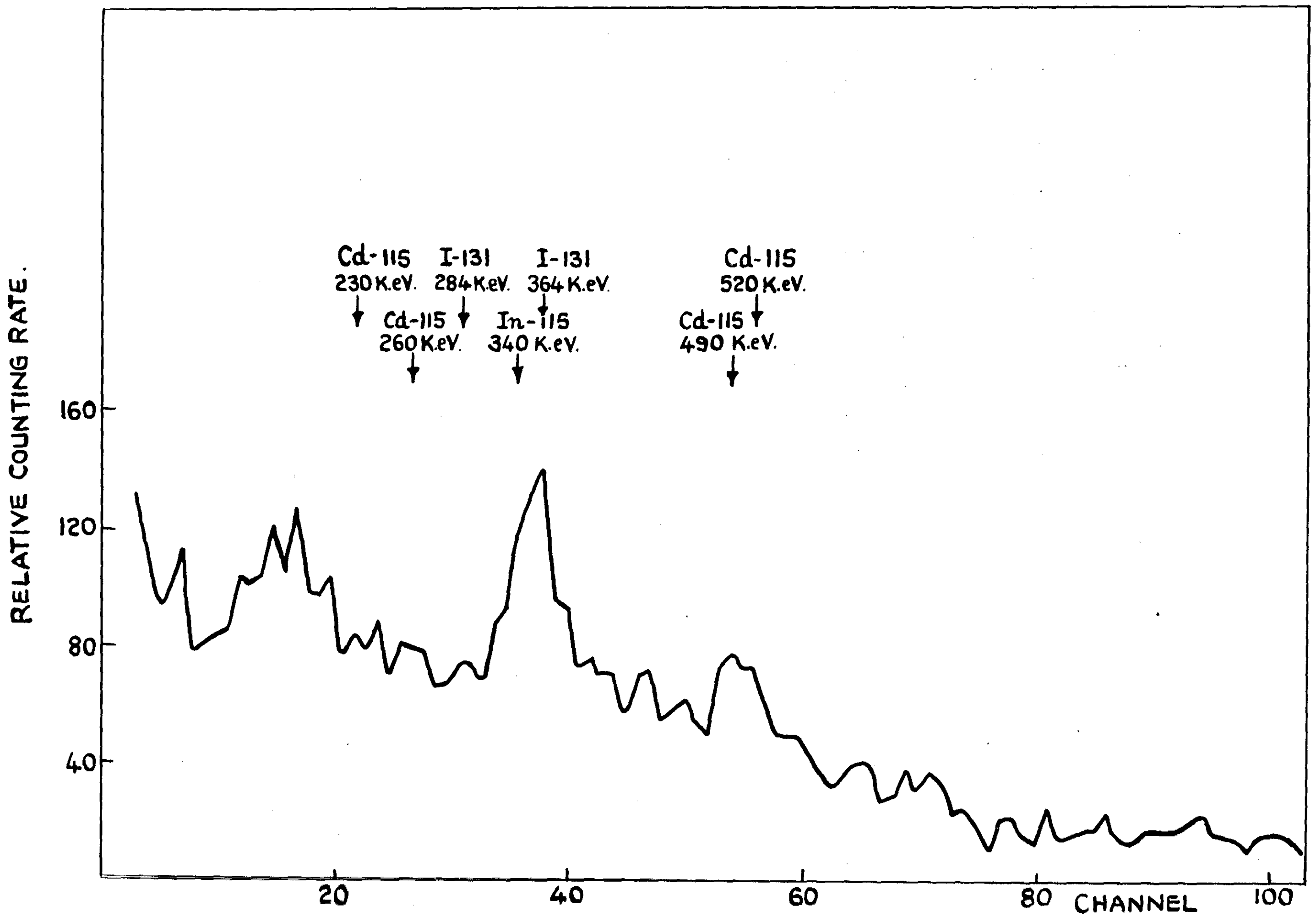
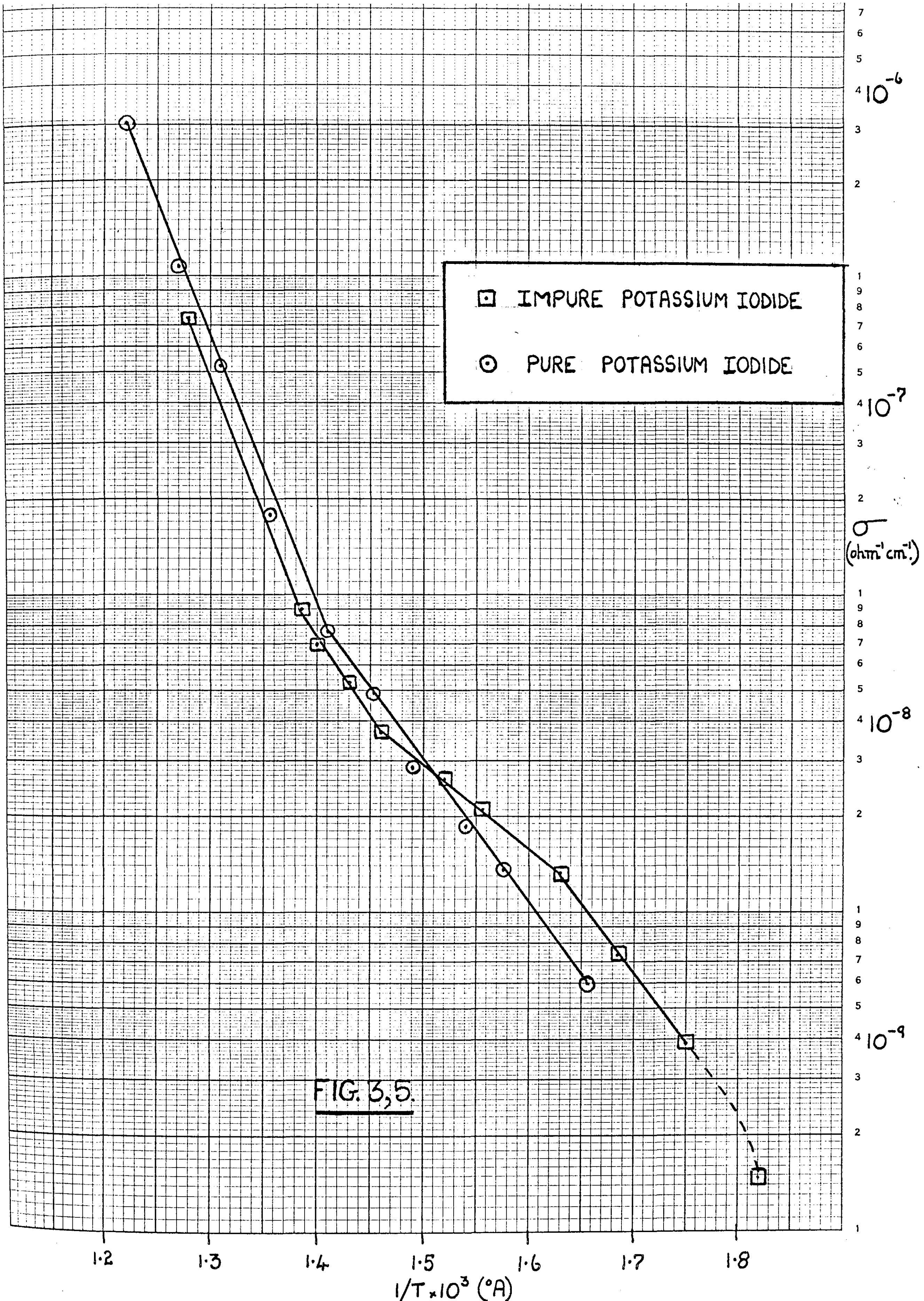

Cd-115
230 K.eV.
Cd-115
260 K.eV.
I-131
284 K.eV.
I-131
364 K.eV.
In-115
340 K.eV.
Cd-115
490 K.eV.
Cd-115
520 K.eV.
RELATIVE COUNTING RATE.
40
80
120
160
20
40
60
80
100
CHANNEL

FIG. 3,4

calculation; this became even more apparent in subsequent work involving pure crystals when the yields greatly improved, and so it was decided to investigate further by determining whether or not the divalent impurity ions previously discovered in these crystals were present in substitutional positions in the potassium iodide lattice; if this were indeed the case, then each divalent metallic ion would create a cation vacancy, and thus enhance the ionic conductivity of the crystal. Thus an ionic conductivity measurement on an impure Macfarlan potassium iodide crystal was made and compared with a similar measurement on a pure Hilger and Watt crystal. It was found, (Figure 3,5), that the former exhibited a sharply defined extrinsic conductivity region, in contrast to the latter, which showed no such region; thus impurity ions occupied substitutional positions in the lattice. Further examination of these impure crystals showed the presence of divalent anion impurity (viz., carbonate and sulphate), also, by analogy with the above, in substitutional positions. This means that they too would create vacancies, but this time in the anion lattice. A recent paper by Swanson and Piercy[3,1] describes how substitutional impurities in gold are capable of blocking focused collision sequences and thereby causing an increase in the observed damage rate. Substitutional



IMPURE POTASSIUM IODIDE
PURE POTASSIUM IODIDE
10^-6
10^-7
10^-8
10^-9
σ (ohm⁻¹ cm⁻¹)
1·2
1·3
1·4
1·5
1·6
1·7
1·8
1/T × 10³ (°A)

FIG. 3,5.

impurities in aluminium had no effect on the damage rate, indicating, as expected, that focused collision sequences in aluminium were unlikely. If these workers had been able to introduce vacancies into close-packed rows, as in the impure potassium iodide, the disruption of the focused collision sequences would have been even more marked. This, we would suggest, is partly the reason for the unexpectedly low yield of recoiled I^{131} from these crystals. The impure crystals used in this work were however unannealed, with a high concentration of dislocations, which would also be instrumental in blocking focused collision sequences. It was therefore decided to perform a comparative irradiation using two annealed Hilger and Watts crystals, one of which had been doped with a divalent anion impurity. Should the latter exhibit a much lower recoil yield, this would constitute strong evidence for the existence of focused collision sequences in this system; furthermore, from a knowledge of the number of vacancies induced and the difference in the recoil yields, we could make an estimate of the number of sequences per (n,γ) event. This proposed experiment had to await the development of efficient collecting systems for I^{131}.

3.2 The Importance of Annealing The Crystals.

Throughout the course of this work, most of the irradiations were conducted in pairs, thus allowing us to check the reproducibility of all the observations. This practice has, in addition, resulted in our noting a significant phenomenon. On labelling the surfaces of two annealed crystals of potassium iodide with I^{131}, one was often found to have a lower surface count rate than the other (as recorded by an end-window G.M. tube). The crystals showing the lower count rates would, on subsequent neutron irradiation, invariably recoil a larger amount of I^{131}-labelled iodine from their surfaces than the others. A typical example of this is the following:

Ratio of Surface Count Rates Before Neutron Irradiation: $\frac{\text{Crystal 'A'}}{\text{Crystal 'B'}} = \frac{1}{3}$

whereas

Ratio of Iodine Recoiled due to Neutron Irradiation: $\frac{\text{Crystal 'A'}}{\text{Crystal 'B'}} = \frac{4}{1}$

This phenomenon can be explained in a qualitative manner as follows:

(a) Annealing improves the ordered crystallographic nature of potassium iodide and, in so doing, smoothes the surface by causing edge dislocations to come together; this means that in the above example, crystal 'B' was less well-annealed than crystal 'A', since it had more surface sites available for exchange.

This is clearly illustrated by the following photomicrographs (final magnification x 850) which show typical areas of crystal 'A' (Plate 3,1) and crystal 'B' (Plate 3,2).

(b) In addition, there would be less chance of focused collision sequences being blocked by dislocations in crystal 'A' than in crystal 'B' (because the former is crystallographically more perfect), thus accounting for the higher yield of recoiled material from the former.

These observations therefore constitute a further piece of indirect evidence for the existence of the postulated focusing effect.

3.3 Cadmium-Shielded Irradiations (Preliminary)

As has been previously noted, the ratio of thermal to fast neutrons in the Central Vertical Stringer of the Reactor is of the order of 5:1. It was thus necessary to verify that the recoils observed in this mixed flux were caused predominantly by (n,γ) thermal neutron interactions. We accordingly irradiated simultaneously, in the Central Vertical Stringer, two I^{131}-labelled small AnalaR potassium iodide crystalline samples, as in Plate 2,6, one of which was covered with a cadmium sheath. Because of the very large absorption

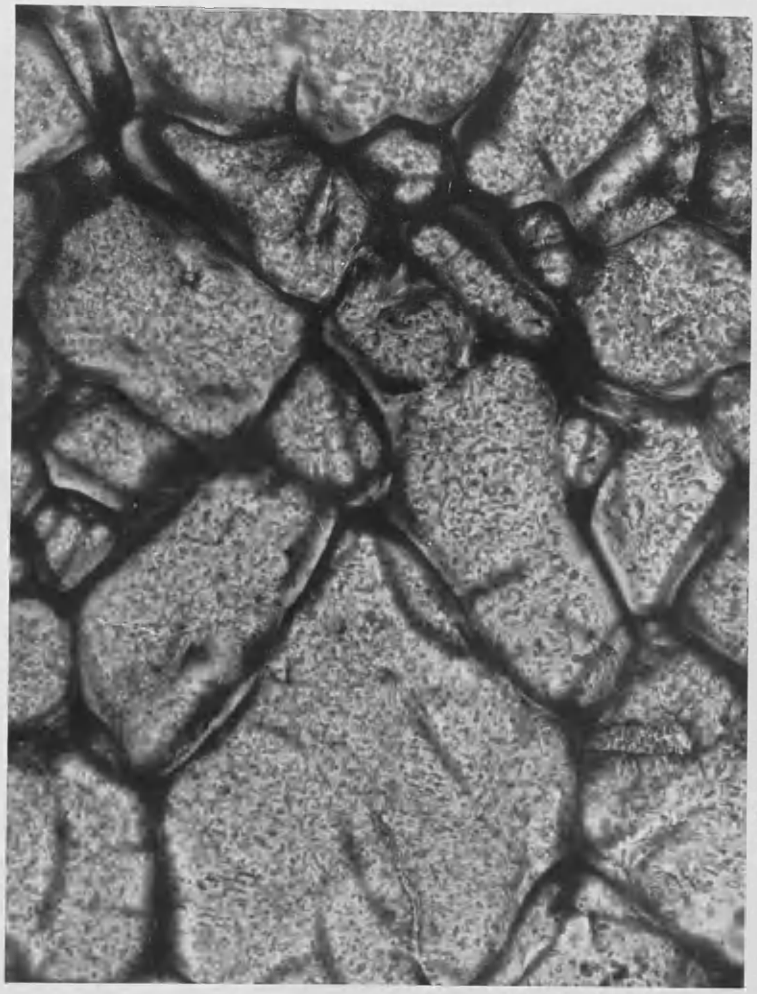


PLATE 3,1

cross-section of cadmium for thermal neutrons, this greatly reduced the thermal neutron flux to which this crystalline specimen was exposed, whilst remaining relatively transparent to neutrons of above 1 eV. in energy. Having performed the experiment on three separate occasions, we found that in every case, the yield of I^{131} recoiled on to the walls of the cadmium-covered tube was smaller than that on the uncovered tube by factors ranging from3 to 10, depending on the length of irradiation and the amount of cadmium used in the shield. This indicated that our initial postulate concerning the likelihood of focused collision sequences being initiated by thermal neutrons seemed to be valid.

3.4 Early Irradiations in the Thermal Column

Having made the above observations, we decided to perform an irradiation of labelled potassium iodide in the Thermal Column of the Reactor, where the Cadmium Ratio is as high as 1,000:1, on the assumption that the absence of fast neutrons would remove the possibility of the production of random energetic recoil species, capable perhaps of defocusing collision sequences. We found, however, that even after an irradiation for four hours at full power, the thermal neutron flux was so much lower than that in the Central Stringer, that only a very small yield of recoiled I^{131} was observed on the walls of the surrounding tubes.

This result prompted us to design a more efficient irradiation system, with which we were able to obtain satisfactory yields of recoiled I^{131} in the Thermal Column, and which we employed to repeat the cadmium-shielded irradiations; both of these experiments will therefore be more fully discussed later, using the more accurate data.

3.5. Preliminary Autoradiographic Results

For this purpose, single crystals of pure potassium iodide were used, for, as has been explained earlier, focusing along the <110> directions of these centrally mounted crystals should produce a series of vertical bands (Figure 2,3) on the inside walls of the tube. Thus, after completion of the irradiation and removal of the crystal, several layers of Ilford 'G' X-ray film were carefully inserted into the tube and allowed to expand against its inside wall. The reason for using more than one layer of X-ray film in each tube was as follows: it had been noticed that in the gamma-ray spectra of the silica tubes (which were of "Vitreosil" quality: Jencons Ltd.) there was present, besides the usual I^{131} peaks, another peak at 0.57 M.eV., due to an impurity in the silica. Not knowing, at this stage, the identity of this impurity, we reasoned that it was unlikely to have the same β-energy, as I^{131}, and would affect the X-ray film to a different extent. If, for example, the film nearest to the tube was uniformly darkened, successive layers would perhaps indicate a pattern.

We found that despite repeated attempts, nothing resembling the postulated pattern could be obtained; some autoradiographs were overall black (Plate 3,3) whilst others showed evidence of a few vertical streaks. Further investigation revealed, however, that such streaks could be obtained by merely irradiating an empty silica tube, leaving it aside for a few days, and inserting X-ray films in the usual way; this indicated that not only had we failed to achieve perfect physical contact between the films and the inside walls of the tubes, but, more significantly, that the background β-activity, due to impurity in the silica, was perhaps of very similar energy to that of I^{131}.

Thus, in order to offer a satisfactory explanation for the above results, it became necessary to identify the impurity present in the silica. This was discovered to be antimony, whose relevant isotopes are tabulated as follows:

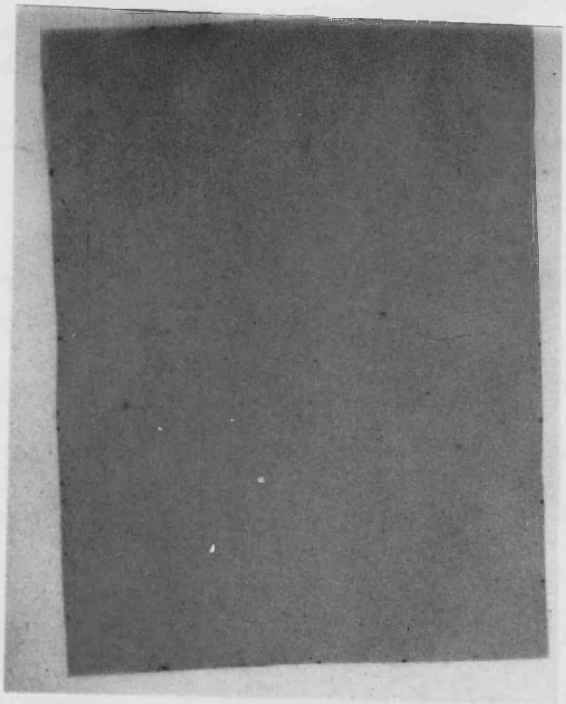


PLATE 3,3

A	%Abundance	Thermal Neutron Absorption Cross Section (Barns)	Radiation	Half-Life	Energy Particles	(M.eV.) γ-Rays
Sb-121 (Stable)	57.25	6.6	-	-	-	-
Sb-122			β, γ, e^-	2.8 days	1.36,1.94	0.57
Sb-123 (Stable)	42.75	2.6	-	-	-	-
Sb-124			β, γ	60 days	0.48,0.65 1.0,1.62, 2.37	0.608

We see from this that the isotope responsible for the gamma-ray peak at 0.57 M.eV. was in fact Sb^{122}. This, however, would have little effect on the autoradiographs, due to its rather high β-energy and relatively short half life, were it not for the fact that it is always accompanied by Sb^{124}, whose average β-energy (0.6 M.eV.) is very much closer to that of I^{131}, and whose half-life is very much longer. Figure 3,6 shows the gamma-ray spectra of two silica tubes, recorded 15 days after irradiation. From this it can be seen how the peak at 0.58 M.eV. has decayed sufficiently to allow the 0.60 M.eV. peak to become apparent. Thus we had a reasonable explanation for the failure of the autoradiography. This diagram can also be used to illustrate a point

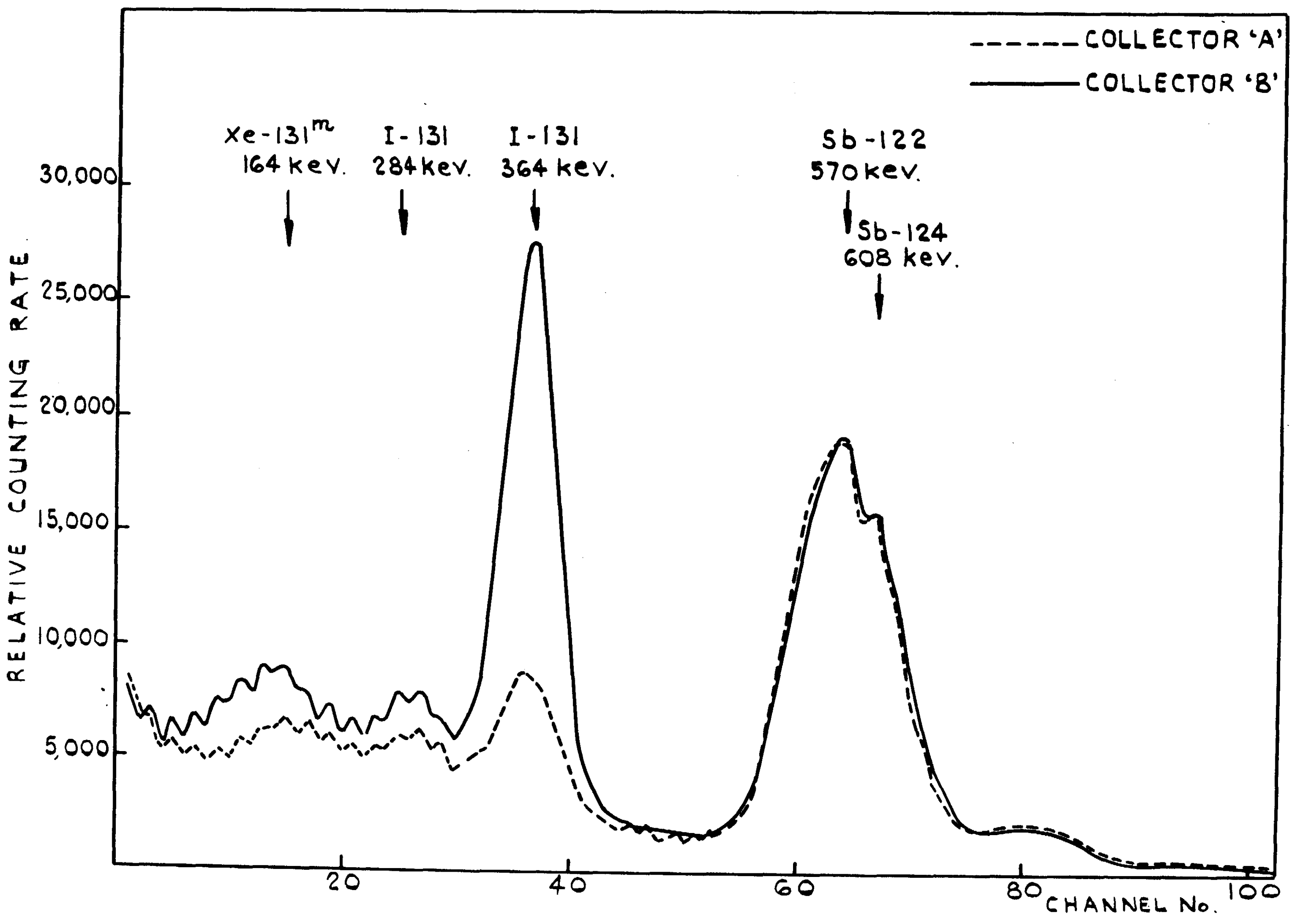

------COLLECTOR 'A'
——COLLECTOR 'B'
Xe-131^m 164 kev.
I-131 284 kev.
I-131 364 kev.
Sb-122 570 kev.
Sb-124 608 kev.
RELATIVE COUNTING RATE
30,000
25,000
20,000
15,000
10,000
5,000
20
40
60
80
100
CHANNEL No.

FIG. 3,6

previously made, concerning the inverse relationship between surface activities of the crystals before irradiation and their subsequent recoiled yields. The average surface activities, recorded by the use of an end-window G.M. tube two days before irradiation, were:

Counts/Min.

Crystal 'A'	Crystal 'B'
28,900	18,100

3.6 The Design and Preparation of an Improved Collecting System

It was now apparent that we could no longer work with a system which involved the iodine being recoiled from the surface of the crystal to the inside wall of a silica tube for the following reasons: firstly, due to the presence of antimony, autoradiography was not feasible, as explained above; secondly, it was realised that there was no particular reason why the iodine, having been recoiled on to the tube, should remain there; some of it could return to the surface of the crystal, with the result that an equilibrium would be established: Nelson and Thompson(3,2) had been obliged to coat their silica collector with aluminium in order to enhance its ability to hold recoiled gold atoms. It thus became necessary to incorporate into our silica irradiation tubes a collector which would have the following properties:

(a) Freedom from impurity and

(b) An ability to combine with recoiling iodine atoms, thus displacing the equilibrium and improving the yield. In addition, such a collector could be removed from the silica vessel after the neutron irradiation, thus greatly simplifying the autoradiographic technique.

It was decided that a thin palladium film, on a suitable inert support, would be the best choice for the following reasons:

(i) Having already utilised the thermal decomposition of palladium iodide and the subsequent recombination of palladium and iodine in our isotopic exchange reaction, we had experience of their ability to combine; this would be further facilitated by the fact that the recoiling iodine was probably in the atomic state.

(ii) Palladium, on thermal neutron irradiation, forms only short-lived products, none of which emit gamma radiation.

The first feature favoured subsequent autoradiography whilst the second meant that the gamma-ray spectrum of the collector would be free from interfering impurity peaks.

As a suitable support for the palladium film, we chose Mylar, which is a strong, commercially available polyethylene terepthalate film; (our films were 0.001"thick). The method by which a thin layer of palladium was deposited on the Mylar film involved the system shown in Figure 3,7. The apparatus, incorporating a length of spectroscopically pure palladium wire (Johnson, Matthey & Co. Ltd.) and a piece of Mylar film (8 in x 4 in) in contact with the inside walls, was placed in a tank of water at 15°C, and evacuated at 10^{-4}Torr. A gradually increasing electric current was then passed through the wire which, on becoming hot, tended to sag; this was prevented by gently rotating the upper B10 cone, thereby winding some of the wire on to the upper tungsten lead. It was found that a current of 6 amps. (at a potential of 4 volts) passed for 10 minutes gave a satisfactory dark film, the central position of the wire ensuring a uniform deposition.

An irradiation of a pair of I^{131}-labelled annealed potassium iodide single crystals was then performed in the Central Vertical Stringer, using the same apparatus as before, but with each silica tube now incorporating a layer of palladium-covered Mylar, held against the insides of the tubes by their own

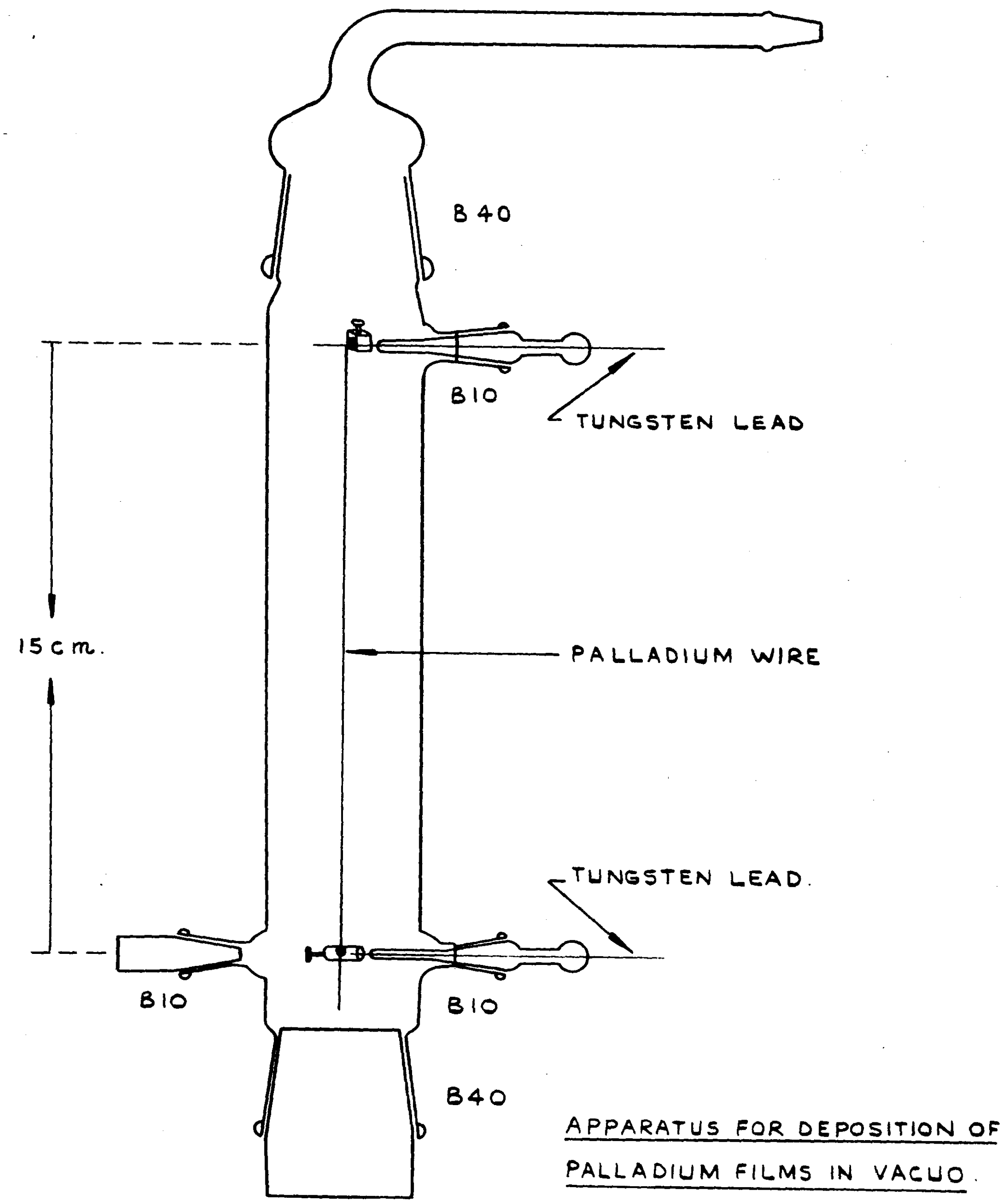

B 40
B10
TUNGSTEN LEAD
15 cm.
PALLADIUM WIRE
TUNGSTEN LEAD.
B10
B10
B40
APPARATUS FOR DEPOSITION OF
PALLADIUM FILMS IN VACUO.

FIG. 3,7

elasticity. After three days, the collector films were removed, placed in separate unused silica tubes (to preserve the counting geometry), and examined in the scintillation counter. It was found that

(a) The yield of collected I^{131} had improved by a factor of approximately 10, thus proving that we had indeed succeeded in our objective to displace the equilibrium in the collector system.

but

(b) Surprisingly, antimony was again present in even greater proportion than in silica. This was as a result of its presence in the Mylar film, having probably been added as one of the constituents of a stabiliser in the manufacturing process. Autoradiographs of these films were therefore black, as expected.

Thus, it became necessary to prepare supporting films which would be free from metallic impurity, and this we succeeded in doing, by using pure polystyrene, supplied by B.X. Plastics Ltd. We found that a solution of polystyrene in chloroform would, if left overnight in a suitable covered dish, yield a transparent polystyrene film; on this, one could deposit a layer of palladium, using the apparatus previously described. We chose polystyrene for this purpose, because(3,3) it is the most radiation-stable common moulding plastic. ("Araldite" is the most radiation-stable adhesive(3,3)).

We repeated the above neutron irradiation experiment, incorporating a palladium-covered polystyrene collector, and obtained not only the same high yield of recoiled I^{131}, but also a gamma-ray spectrum which was entirely free from any impurity peaks, shown in Figure 3,8. This improvement in yield allowed us to reduce subsequent irradiation times from four hours to one hour. The collector films were then exposed to Ilford 'G' X-ray film, but the resultant autoradiographs were again uniformly black, indicating that the I^{131} was distributed uniformly over their entire area; this was proved by dividing each collector film into four equal portions, and recording their gamma-ray spectra in turn. This remarkable uniformity of distribution of the I^{131} immediately suggested that it was mobile on the palladium surface; such phenomena are well known in the study of catalysis - for example, Robell et al(3,4) have recently shown that chemisorbed hydrogen can migrate across a platinum surface on to a carbon support.

3.7 An Alternative Collecting System

It was decided that one method of clarifying this problem would be to utilise a collector system whose ability to combine with iodine depended on an

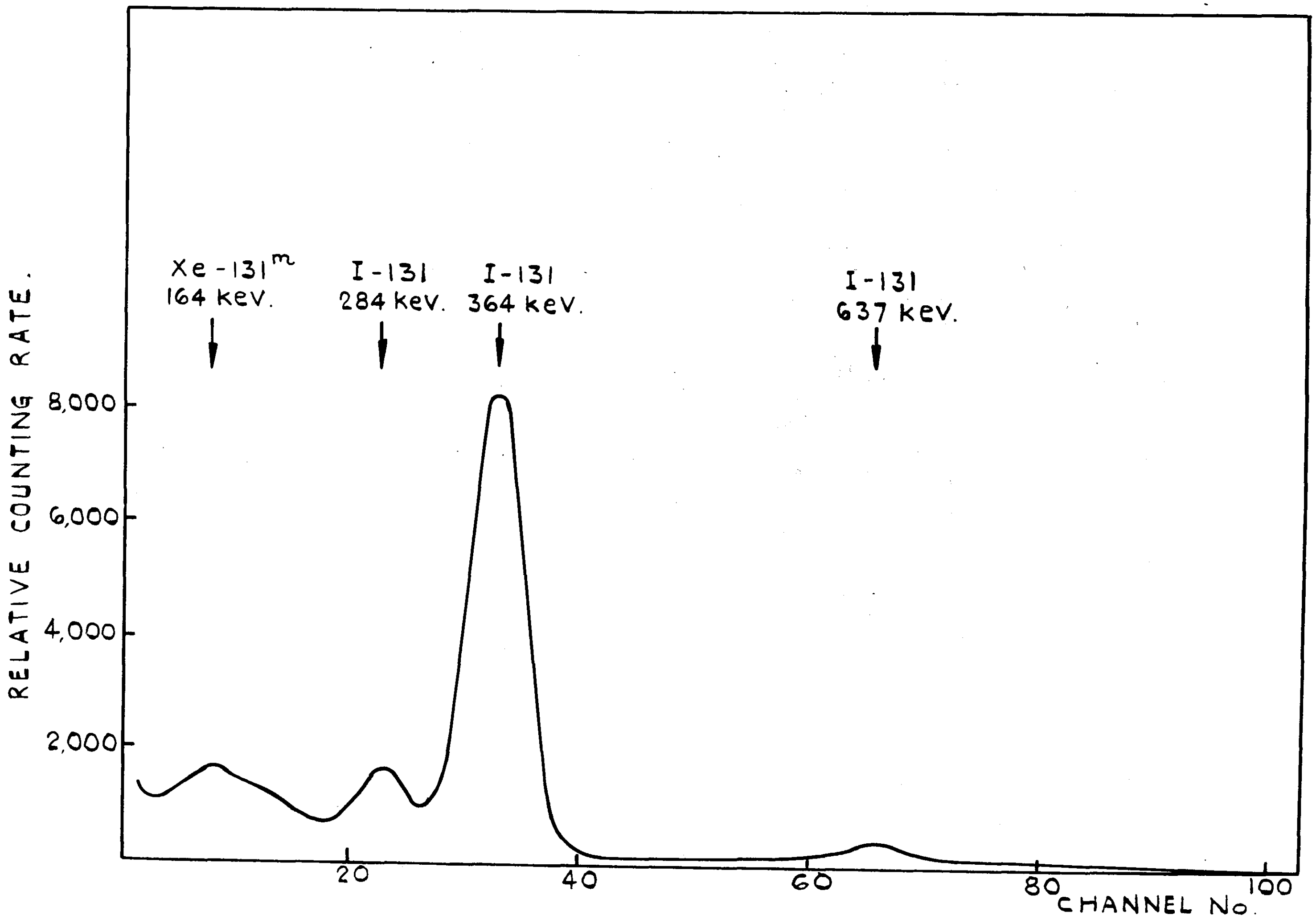

Xe-131^m
164 keV.
I-131
284 keV.
I-131
364 keV.
I-131
637 keV.
RELATIVE COUNTING RATE.
8,000
6,000
4,000
2,000
20
40
60
80
100
CHANNEL No.

FIG. 3,8

entirely different principle. We therefore investigated a polymer which incorporated double-bond ethylenic linkages for the following reasons:

(a) Wolfgang's group at Yale University have shown(3,5) that 'hot' atomic carbon atoms are capable of combining with ethylenic linkages.

(b) Chemical kinetics indicate that the addition of halogens to double bonds proceeds via a free radical mechanism, and therefore should be very likely for a halogen in the atomic state.

Having tested various polymers of this type for ease of preparation and stability, we chose a butadiene-acrylonitrile co-polymer ("Butakon", I.C.I. Ltd.) which could be prepared as a film from chloroform solution in the same way as polystyrene. Since it had very little elasticity, and would therefore have been unable to hold its position against the inside walls of a tube, it was bonded with chloroform to a piece of polystyrene (to act as a support), thus allowing it to be easily inserted into the irradiation tubes, and was then used without further modification.

Having employed this film as a collector in another neutron irradiation of labelled potassium iodide, we found that not only was its gamma-ray spectrum entirely free from interfering impurity, but, if anything, it was an even more efficient collector than palladium. However, it was discovered, from autoradiographic and scintillation counting scanning techniques, that the I^{131} was again uniformly distributed over its entire surface.

3.8 The Shielding Experiments

This even deposition of I^{131} over the surfaces of two different types of collecting systems forced us to examine the possibility that the recoiled iodine was being randomly scattered in the course of its passage from the crystal surface to the collector, due to an insufficiently good vacuum in the irradiation tube. The vacuum in these tubes immediately prior to sealing off from the high vacuum pumping system was of the order of 10^{-4} Torr., at which pressure the mean free path between successive collisions would be 50 cm.(3,6); since the maximum distance which any recoiled iodine atoms would have to travel before reaching the collector system was less than 2 cm., this would appear to have been adequate. This argument fails to take account of the fact that as soon as the tubes have been sealed off from the vacuum pumps, slow de-gassing from the walls would begin; and the situation would be aggravated in the Reactor, where, under the influence of neutron and gamma irradiation, such de-gassing would be accelerated. The result would be that the mean free path would be less than envisaged.

To test the validity of these ideas, we designed an experiment in which the top quarter of a palladium-covered polystyrene collector (see Figure 2,3) was shielded with another piece of palladium-covered polystyrene and placed in a silica tube with an annealed I^{131}-labelled potassium iodide crystal. The system was then evacuated overnight, sealed off, and irradiated in the Central Vertical Stringer for one hour.

The idea was that if gas scattering was responsible for the overall distribution of recoiled iodine on the collector, then the shield should collect about one third as much I^{131} as the larger film, the top quarter of which should be relatively free from I^{131}; on the other hand, if surface mobility was indeed the predominant mechanism, then the shield should collect less than one quarter as much active species as the larger film, and the I^{131} should be spread over the entire surface of the latter.

After neutron irradiation, the shield and larger film were removed, the latter being divided into four quarters, and the gamma-ray spectra of all of them recorded. It was found that

(a) Each quarter of the large film, including that which had been shielded, had almost exactly the same amount of I^{131} on its surface, indicating mobility over the entire surface.

(b) The shield had collected almost as much I^{131} as each quarter, thus suggesting that a considerable amount of gaseous scattering had taken place.

Similar results were obtained when this experiment was repeated, using an ethylenic polymer film and shield.

It was thus indicated that not only was the vacuum in the irradiation vessels unsatisfactory, but that the iodine seemed to be capable of movement over the surface of the collector. (Experiments to be described later, suggest a more precise reason for the latter phenomenon).

3.9. An Improved Vacuum Irradiation System

In view of these conclusions, it was necessary to improve the vacua in the silica tubes during neutron irradiation, and this we did by extending the tubes, to allow them to accommodate activated charcoal. Irradiations were performed with the whole system surrounded by solid carbon dioxide ('Drikold'), for activated charcoal is an efficient sorption pump, particularly when refrigerated(3,7). The cooling influence of the Drikold should also reduce thermal lattice vibrations in the potassium iodide, thereby improving the propagation of focused collision sequences, and increase the yield of recoiled iodine; its presence might also lead to a reduction in the surface migration of iodine on the collector.

Preliminary tests established that Picien Wax did not lose its vacuum-holding properties in the presence of Drikold and that the Drikold lasted for fully two hours.

The experimental procedure was as follows:

Activated charcoal (Sutcliffe, Speakman & Co. Ltd.) was initially baked out at 350°C for 12 hours, after which it was cooled under vacuum to room temperature, and transferred to the irradiation vessel shown in Figure 3,9. (The wad of silica wool was placed in position to prevent the entry of charcoal dust into the side arm during the bake-out, since this causes embrittlement of the silica at the point where the side arm is subsequently sealed off, with consequent risk of leakage). The collector film was then inserted, and the annealed I^{131}-labelled single crystal of potassium iodide fitted into the tube by means of Picien Wax. The charcoal was then baked out in situ at 140°C over the next two days, and the resultant de-gassing followed on a McLeod gauge; during this time the heat-sensitive collector

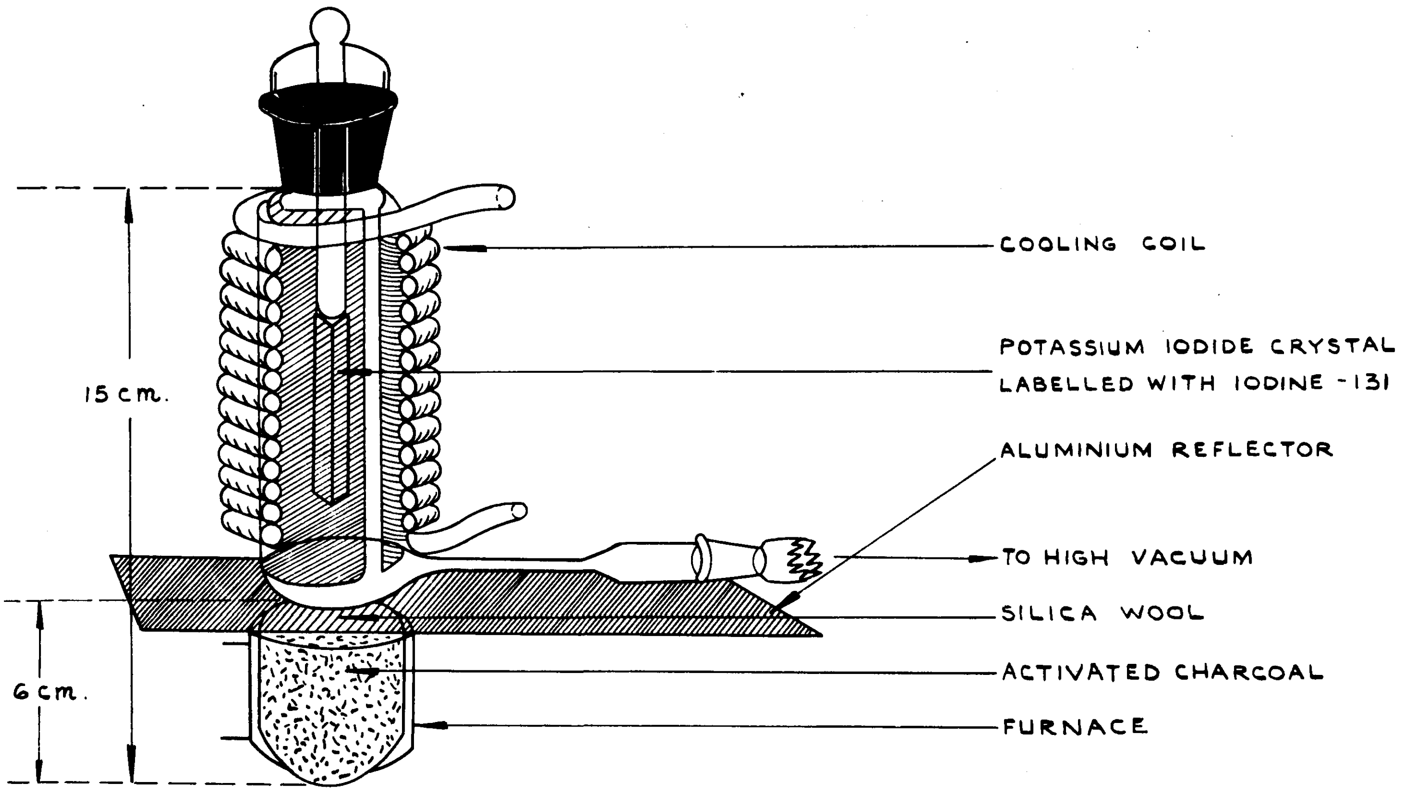


DIAGRAM OF SYSTEM DURING BAKE-OUT.

FIG. 3,9

film was protected by means of the cold water cooling coil and aluminium heat reflector. At the end of the bake-out period, the furnace, reflector and cooling coil were removed, and the system sealed off under vacuum. It was then packed in a Polythene bottle with Drikold, ready for irradiation.

This method proved to be a considerable success, for not only did the yield of recoiled iodine improve by a further factor of three, but, for the first time, autoradiographic and gamma-ray scintillation scanning techniques showed a localisation of I^{131} in the form of a band on the collector film: a typical autoradiograph is shown in Plate $3{,}4^{1}$. Thus, although we had not yet obtained a striated pattern, this was an encouraging result.

It was observed that in this system the palladium-polystyrene collector films were now considerably more efficient than the unsaturated polymer ones, although their autoradiographs also showed a similar "band" (Plate $3{,}4^{2}$); and thus the latter were abandoned in the meantime.

Efforts were now directed towards an understanding of why the recoiled I^{131} was collected in the form of a band, rather than in a series of discrete vertical lines. We soon discovered, however, that the reason for this was perhaps connected with a rather remarkable

PLATE 3,4^I

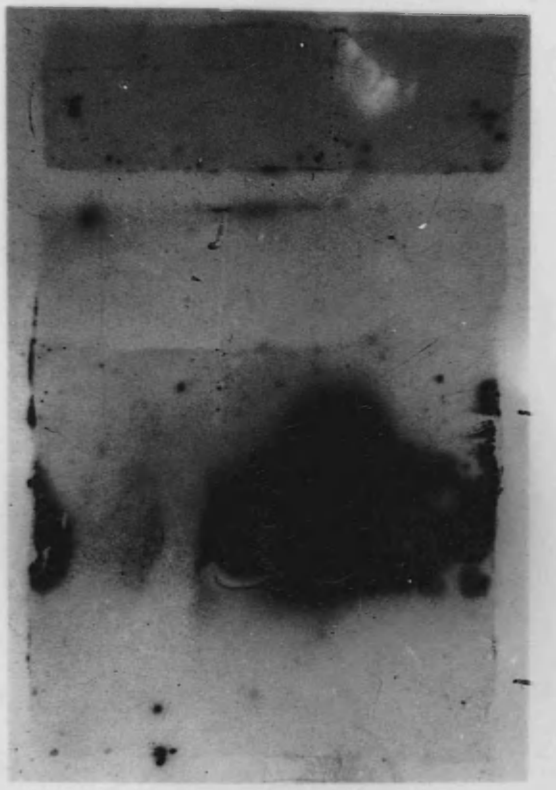


PLATE 3,4^2

alteration in the gamma-ray spectra of the recoiled material, which shall now be described in some detail.

3.10 The Distorted Gamma-Ray Spectra

Before using the improved irradiation system incorporating activated charcoal and Drikold, we had developed collector films which, after irradiation, yielded impurity-free gamma-ray spectra of the type shown in Figure 3,8. By comparing this diagram with the decay scheme shown in Figure 3,2, it may readily be seen that the principal mode of decay of I^{131} is via a 0.364 M.eV. transition.

It was found that the gamma-ray spectra of collector films used in our improved irradiation system were quite different, having the appearance shown in Figure 3,10 where the same peaks are present as in Figure 3,8, but their relative ratios are substantially altered; for this reason, such spectra shall be referred to as 'distorted' spectra.

In a preliminary investigation, each collector film was cut horizontally into four quarters which were examined in turn in the scintillation counter; from this it was found that the 0.364 M.eV. peak was localised in the manner that one would have predicted from the autoradiograph shown in Plate 3,4[1]; but so were the other peaks, and indeed to a greater

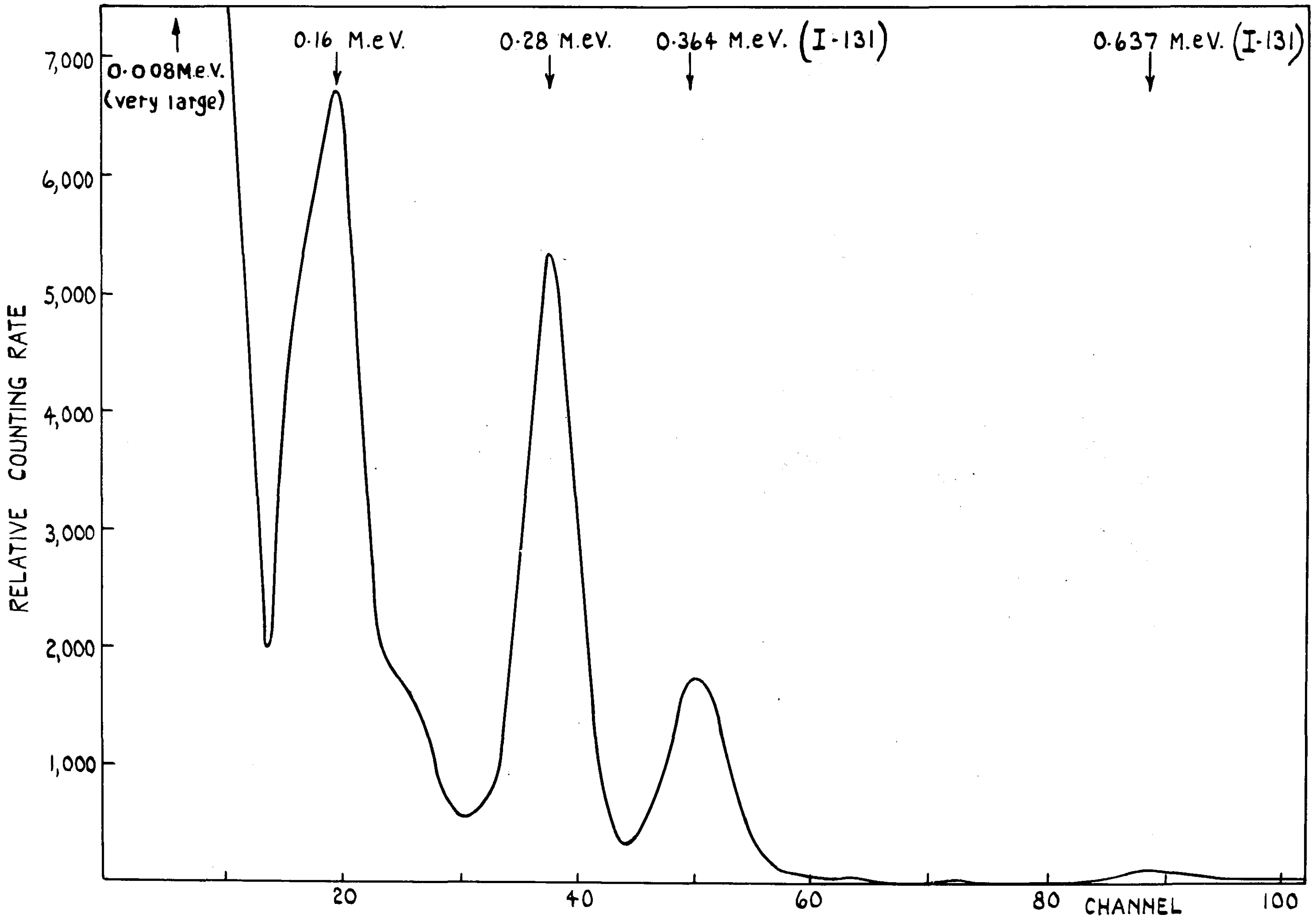

0·008M.e.V. (very large)
0·16 M.e.V.
0·28 M.e.V.
0·364 M.e.V. (I-131)
0·637 M.e.V. (I-131)
7,000
6,000
5,000
4,000
3,000
2,000
1,000
RELATIVE COUNTING RATE
20
40
60
80
100
CHANNEL

FIG. 3,10

extent, than the 0.364 M.eV. peak. (as shown in the Table below which utilises the 0.28 M.eV. peak to typify the distribution of the extra peaks)

Integrated Counts

(Summed over 5 Channels, and Corrected for Neighbouring Peak Influence)

	0.28 M.eV. Peak	0.364 M.eV. Peak
1st Quarter	1,498	117
2nd Quarter	1,912	118
3rd Quarter	12,609	252
4th Quarter	2,849	129

This was confirmed by the fact that the exposure time required for this autoradiograph was only one hour, this being very much shorter than that which would have been calculated from the abundance of pure iodine present, based on the 0.364 M.eV. peak height. More significantly, it emphasised that the extra peaks were not due to impurity in the collector films. It should be noted that distorted spectra were observed on both palladium-polystyrene and unsaturated polymer collector films.

Preliminary examination of these distorted spectra by scintillation counting at intervals over several weeks proved that the 0.364 M.eV. peak decayed with its expected half-life of 8 days, but that the other peaks had different decay rates: in particular, the peak at 0.28 M.eV. seemed to have a half-life of the order of 50 days. (The method by which all of these half-lives were characterised will be described later).

Careful checks were made on the scintillation counter and pulse height analyser; these indicated that our observations were valid.

As a further investigation of the effect, we turned our attention to the potassium iodide crystals: in order to check against the possibility of the extra peaks being in some way connected with irradiations performed in the presence of Drikold, a pure crystal of potassium iodide was annealed and labelled with I^{131} in the usual way, then packed into a Polythene bottle with Drikold, and irradiated in the Central Vertical Stringer. On subsequent examination, it was found to exhibit a perfectly undistorted I^{131} spectrum. A similar irradiation in Drikold of a pure, annealed, unlabelled potassium iodide crystal was performed to check against the possibility of the extra peaks having come from a trace inpurity, which was being selectively removed from the crystal by irradiations performed in our Drikold - activated charcoal system. This crystal showed very little induced activity, most of which had disappeared within a few days. In addition, several of the I^{131}-labelled potassium iodide crystals, which had yielded distorted spectra were examined in the scintillation counter at intervals over a period of several weeks. They were all found to exhibit pure I^{131} spectra which decayed with the expected half-lives of 8.06 days (except, in each case, the peak at 0.16 M.eV. due to Xe^{131m}, which, as expected, showed a 12 day half-life).

The charcoal sorption pump would be expected to collect any iodine scattered from the collector film during neutron irradiation. On subsequent examination in the scintillation counter, it was in fact invariably found to be highly radioactive, exhibiting a distorted spectrum, in which the extra peaks were in far greater abundance than those on the collector films. We thus prepared a charge of activated charcoal, sealed it in a silica tube, packed it into a Polythene bottle with Drikold, and irradiated it in the Central Vertical Stringer, to act as a 'blank'. On subsequent examination (see Figure 3,11), it exhibited very little induced activity, compared to that which would be shown by a similar charge used as a sorption pump.

Examination of the literature(3,8) failed to reveal any evidence of such distortion in the I^{131}

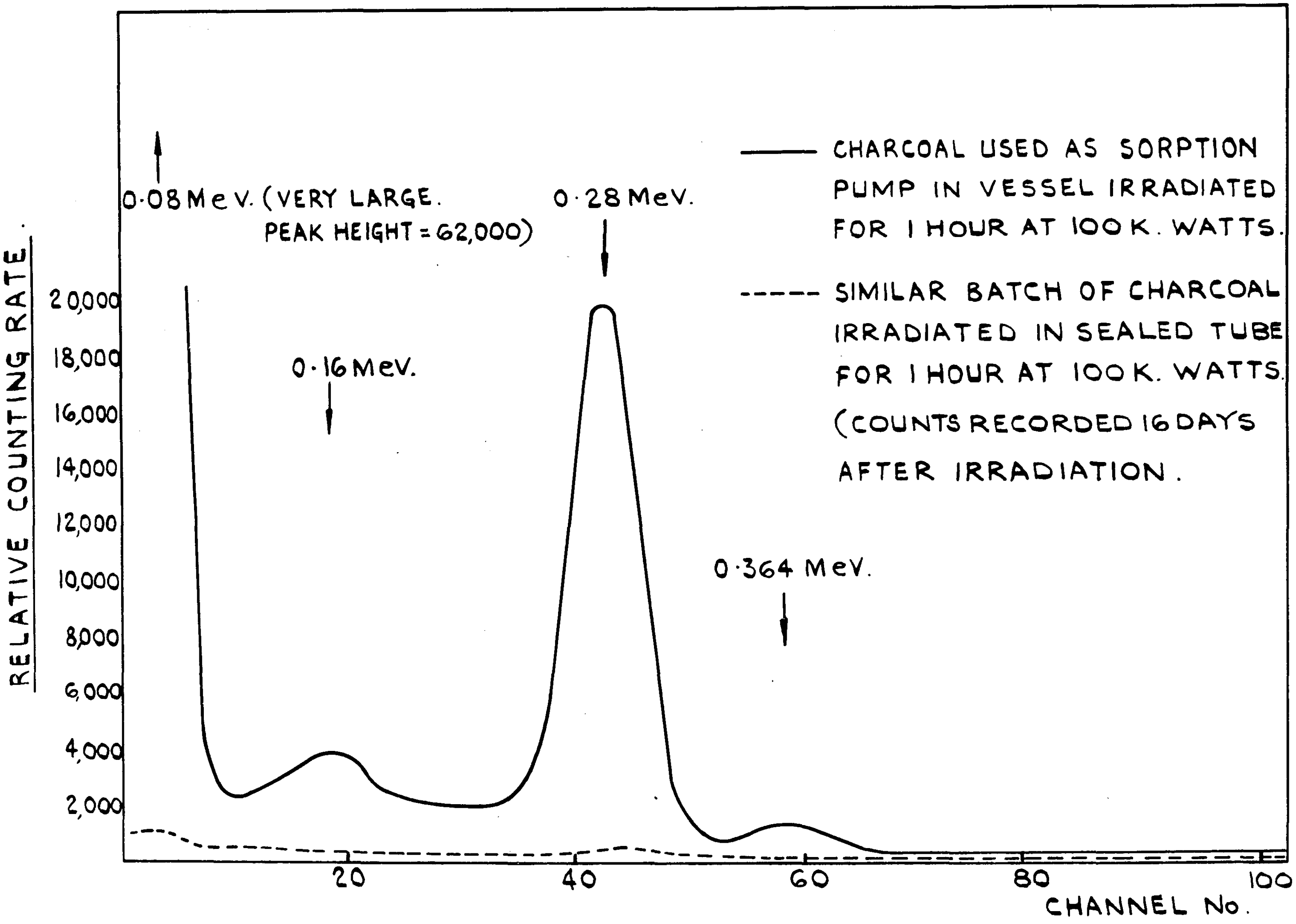

0·08 MeV. (VERY LARGE.
PEAK HEIGHT = 62,000)
0·16 MeV.
0·28 MeV.
0·364 MeV.
CHARCOAL USED AS SORPTION PUMP IN VESSEL IRRADIATED FOR 1 HOUR AT 100 K. WATTS.
SIMILAR BATCH OF CHARCOAL IRRADIATED IN SEALED TUBE FOR 1 HOUR AT 100 K. WATTS. (COUNTS RECORDED 16 DAYS AFTER IRRADIATION.
RELATIVE COUNTING RATE
20,000
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
20
40
60
80
100
CHANNEL No.

FIG. 3,11

gamma-ray spectrum having been reported before.

In view of the very high yields of recoiled material collected by the activated charcoal - Drikold system, we were then able to reduce the Reactor irradiation time from one hour to five minutes. Subsequent examination showed the gamma-ray spectrum of the collector to be rather less distorted than before, but its autoradiograph (Plate 3,5) was curious. This will be discussed later.

The improvement in yields allowed us to repeat two sets of experiments which have been briefly described, viz., the Cadmium-Covered Irradiations and the Thermal Column Irradiations. These experiments confirmed that the yields of I^{131} recoiled on to collector films (as measured by the 0.364 M.eV. peak areas on the corresponding gamma-ray spectra) depended on the thermal neutron flux. In addition, the Thermal Column Irradiations gave a clue towards an understanding of the distorted spectra effect, as described below:

3.11 The Repeated Cadmium-Shielded Irradiations

One of the irradiation systems shown in Figure 3,9 was baked out in vacuo, sealed off, covered with a sheath of cadmium, and placed in a Polythene bottle along with a similar uncovered system. They were completely surrounded by Drikold, and irradiated in

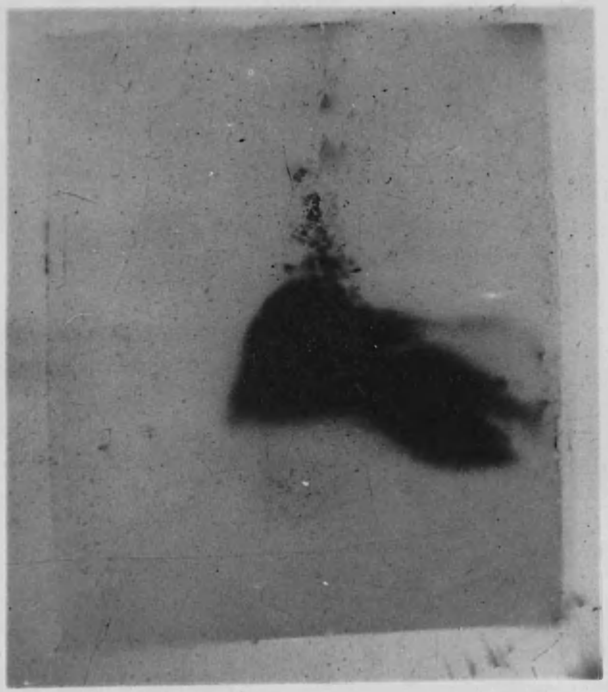


PLATE 3,5

the Central Vertical Stringer in a flux of 10^{12} neutrons/cm^2/sec. for 5 minutes. Three days later, the palladium-polystyrene films were removed, and their gamma-ray spectra recorded, as shown in Figure 3,12.

Not only did the yield of recoiled iodine fall (by approximately a factor of 5) as compared to that from similar irradiations conducted in the absence of cadmium, but there was a drop in the yield of I^{131} collected in the uncovered tube, due to its close proximity to the cadmium shield.

These results agree with the cadmium-shielded irradiation previously conducted under less efficient experimental conditions.

3.12. The Repeated Thermal Column Irradiations

The apparatus used is shown in Figure 3,13. The tubes shown here, which had previously been prepared for irradiation in the usual way, were placed in the Polythene container, completely surrounded by Drikold, covered with a Polythene lid, and slid (in the indicated direction) into the horizontal Thermal Column. There they were irradiated at full power for one hour.

The gamma-ray spectra of the palladium-polystyrene collector films, recorded three days later, are shown in Figure 3,14, from which the following observations were made:

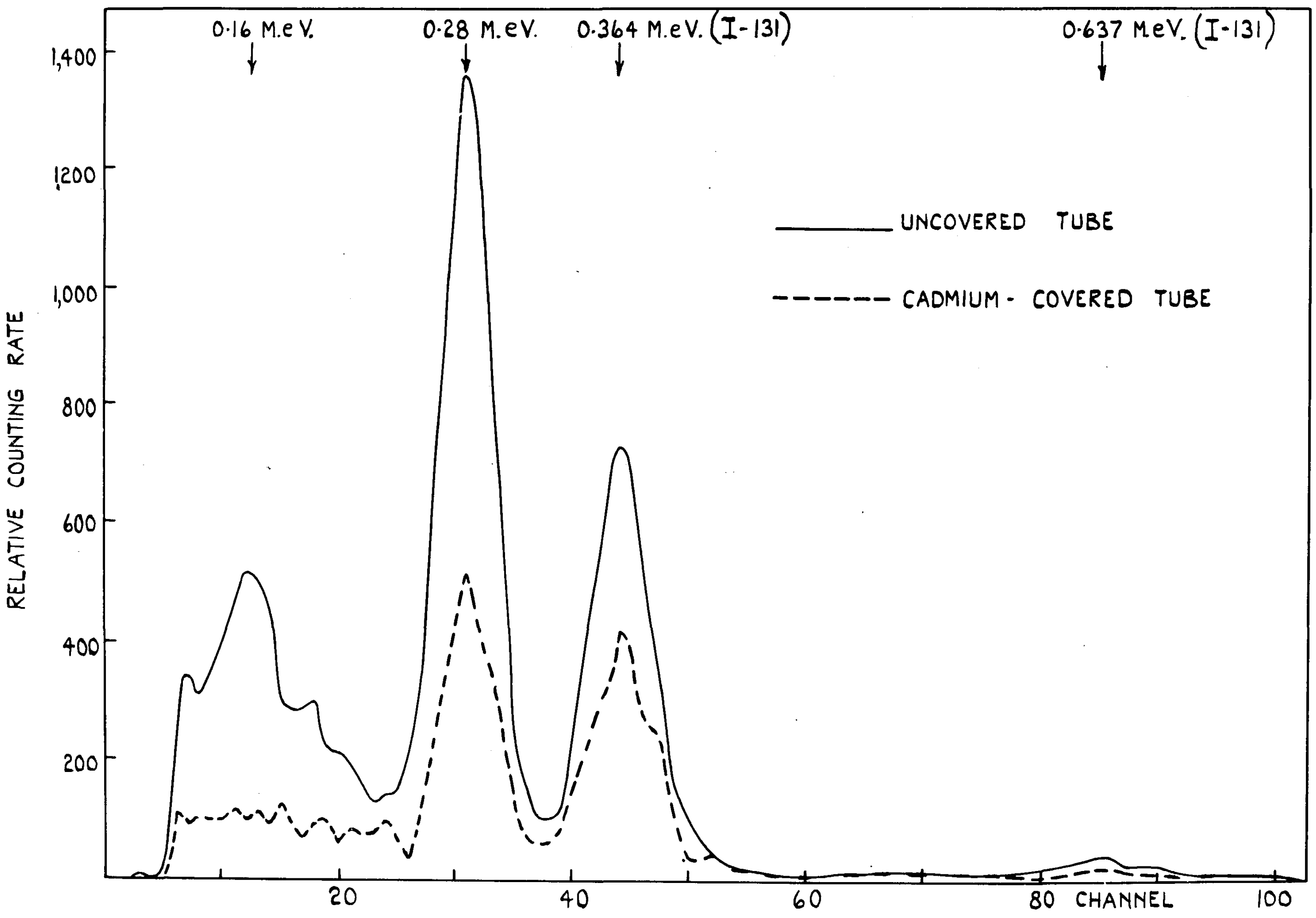
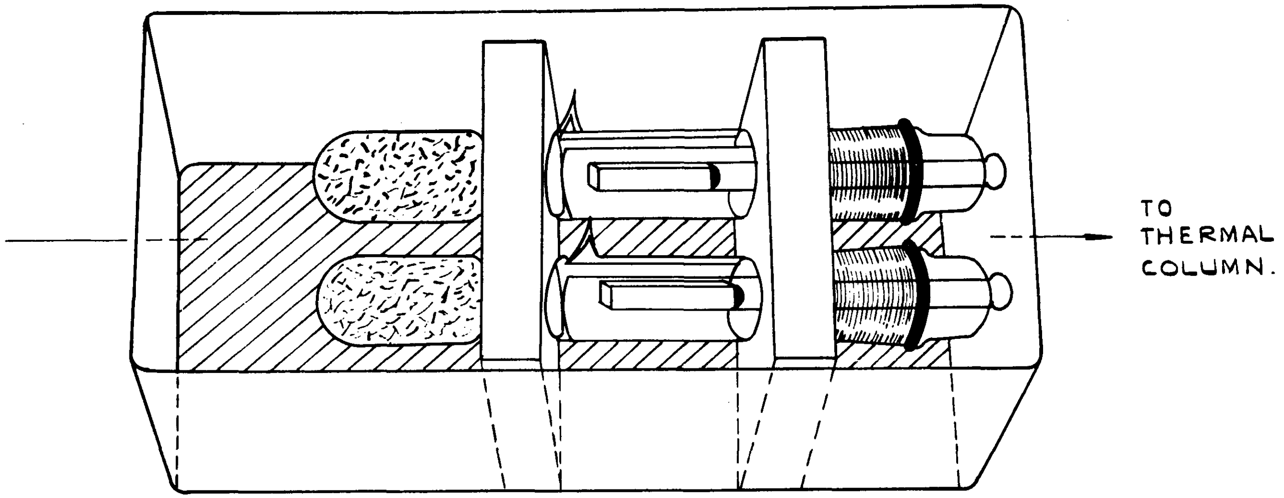

0·16 M.e.V.
0·28 M.e.V.
0·364 M.e.V. (I-131)
0·637 M.eV. (I-131)
1,400
1200
1,000
800
600
400
200
RELATIVE COUNTING RATE
UNCOVERED TUBE
CADMIUM - COVERED TUBE
20
40
60
80
CHANNEL
100

FIG. 3,12



ARRANGEMENT OF TUBES FOR THERMAL COLUMN IRRADIATION.

FIG. 3,13

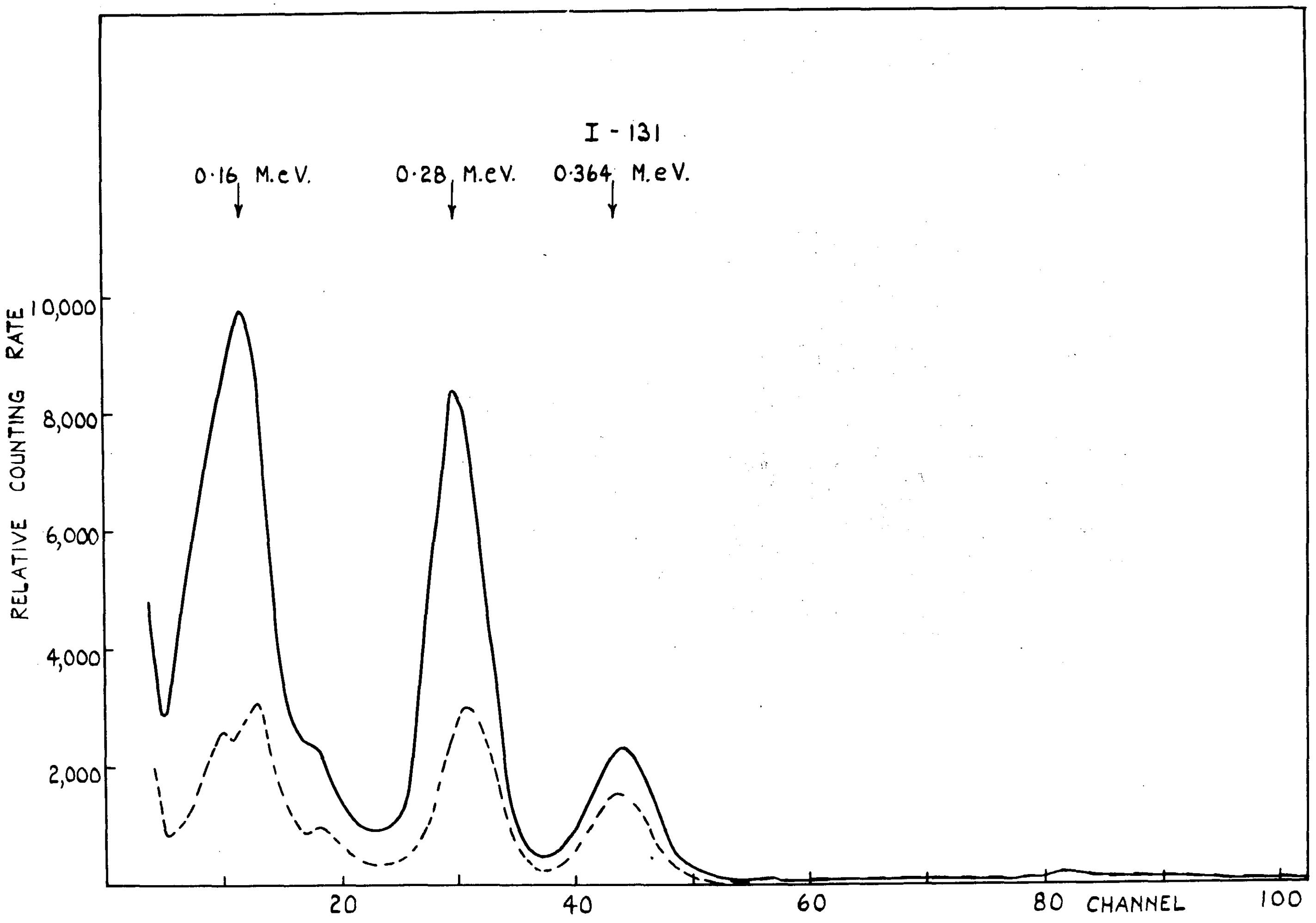

I - 131
0·16 M.eV.
0·28 M.eV.
0·364 M.eV.
RELATIVE COUNTING RATE
10,000
8,000
6,000
4,000
2,000
20
40
60
80
CHANNEL
100

FIG. 3,14

(a) Although the average neutron flux in this region of the Thermal Column was found, using gold foil dosimeters, to be 1.4 x 10^{11} neutrons/cm^2/sec., which was lower, by almost a factor of 10 than that measured in the Central Vertical Stringer (1.2 x 10^{12} neutrons/cm^2/sec.), the yields of recoiled iodine, as measured by the 0.364 M.eV. peak area, were almost half as great. This seemed to verify our earlier postulate that the presence of fast neutrons can exert a detrimental effect on the yields.

(b) One of the gamma-ray spectra (full line, (A)) is more distorted than the other (dotted line, (B)). Autoradiographs of these collector films showed a dark band in a position approximately opposite the crystal in the case of film B (Plate 3,6), whereas, most surprisingly, the band on film A was concentrated in its top quarter (Plate 3,7) - i.e. was no longer localised in a position opposite the crystal.

Preliminary Explanation for the Above Effect

The method of preparation of the polystyrene films resulted in their containing occluded chloroform; although some would be removed in the pre-irradiation evacuation, the films could still be capable of de-gassing on subsequent neutron irradiation. The

PLATE 3,6

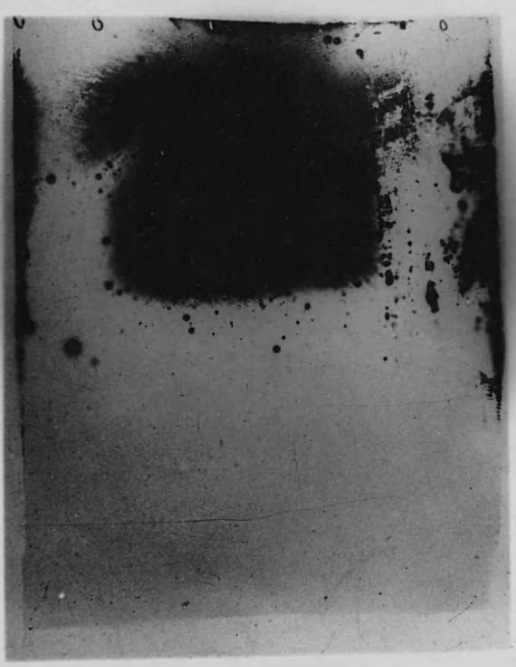


PLATE 3,7

neutron flux in the Thermal Column falls off steeply along its length; this means that the irradiation vessels in Figure 3,13 were subjected to a neutron flux which decreased sharply from right to left; this in turn means that the top regions of the collector films should be de-gassing more quickly than the remainder. There thus appeared to be a connection between the extent to which films are de-gassing during irradiation and their abilities to collect recoiled material.

This connection leads to the experiments described in 3.13.

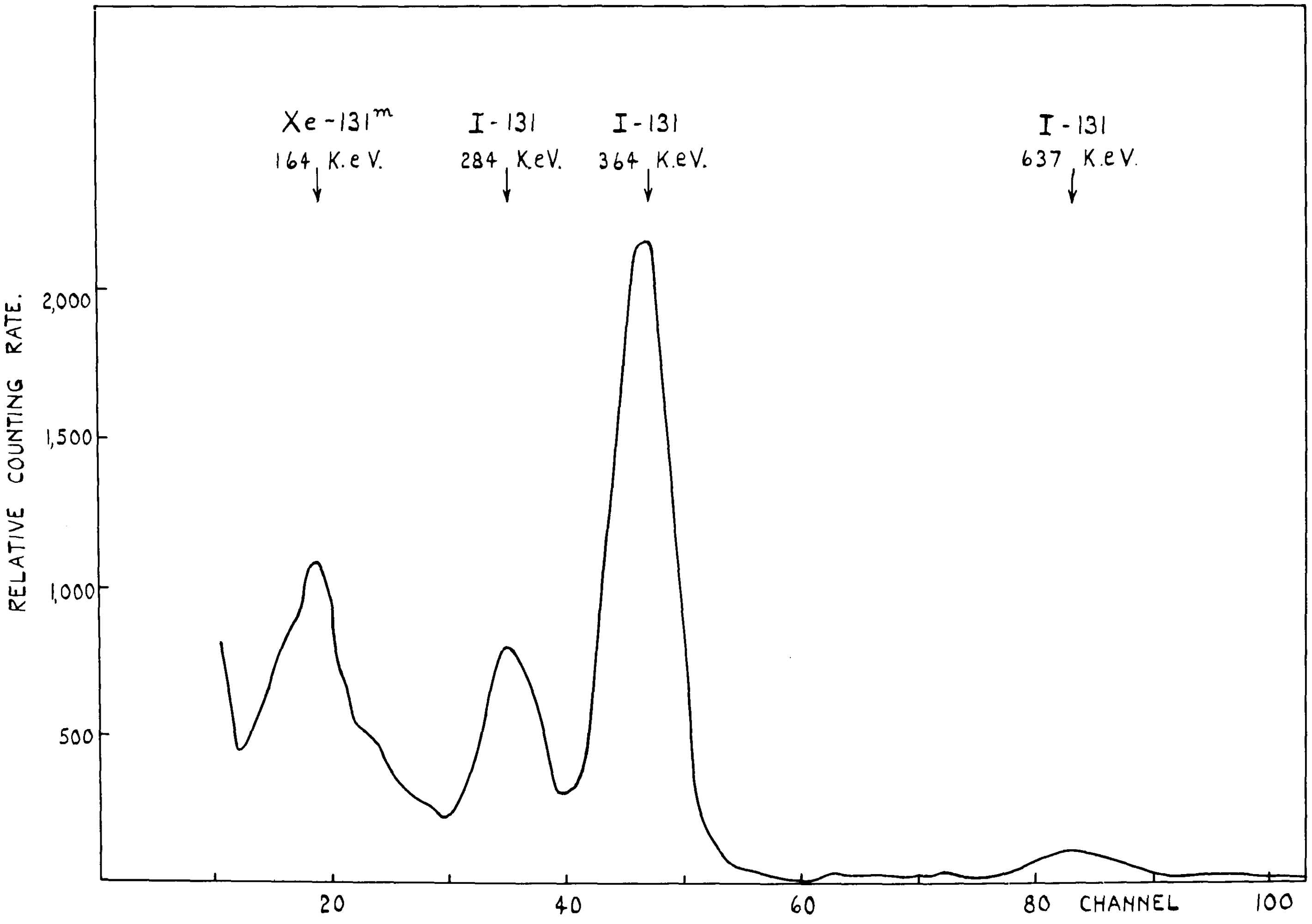
3.13. An Irradiation Experiment Incorporating A Previously De-Gassed Collector Film.

A neutron irradiation was conducted in the Central Vertical Stringer, using the system shown in Figure 3,9, which was surrounded as usual by Drikold, but incorporating a palladium-polystyrene film which had been de-gassed in vacuo at 34°C for 12 hours.

On subsequent examination of the gamma-ray spectrum of the film, shown in Figure 3,15, it was found that the gross distortion had been largely eliminated; it now resembled the pure I^{131} spectrum. The autoradiograph was similar to that shown in Plate 3,6.

3.14. Surface Changes Effected On De-Gassing Collector Films In Vacuo

Plate 3,8 shows a photomicrograph (final magnification x 850) of the collector film used to give



Xe-131^m
164 K.e V.
I-131
284 K.eV.
I-131
364 K.eV.
I-131
637 K.eV.
RELATIVE COUNTING RATE.
2,000
1,500
1,000
500
20
40
60
80
CHANNEL
100

FIG. 3,15

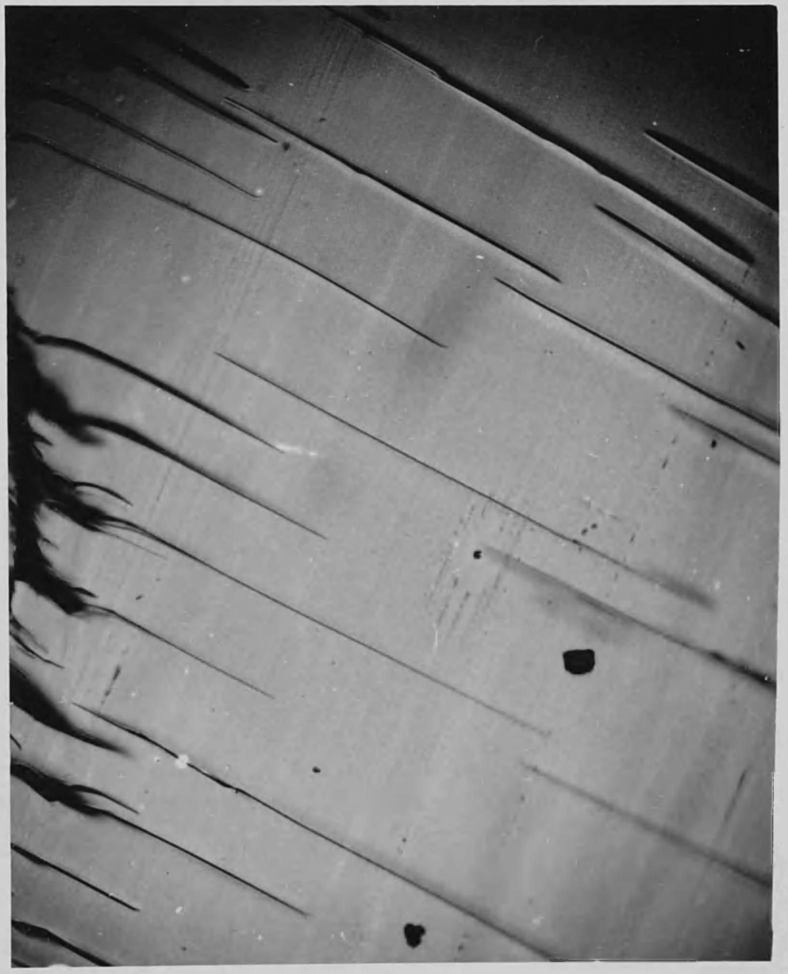


PLATE 3,8

the autoradiograph shown in Plate 3,4; this film had been protected by cooling coils during the pre-irradiation bake-out. On the other hand, Plate 3,9 (final magnification x 850) shows the previously-degassed collector film described above; in this case, the palladium surface has been seriously disrupted, presumably due to shrinkage of the polystyrene film on heating. This may have rendered the palladium less efficient as an iodine collector, since, in addition to the inconclusive autoradiograph, the amount of iodine collected was smaller than would have been expected.

3.15. De-Gassing of Palladium-Polystyrene Collector Films By Prior Neutron Irradiation

As a test of the validity of the hypothesis that film degassing affects the yields, etc., it was decided to use neutron irradiation to de-gas the collector films before use; this would have the advantage of preventing any gross damage to their palladium surfaces.

The method used was as follows: two palladium-polystyrene films were placed in separate irradiation vessels (with activated charcoal which had previously been de-gassed at 350°C for 12 hours) and evacuated, with cooling, (Figure 3,9) whilst the activated charcoal was further baked out at 120°C over a period of two days. They were then sealed off, and irradiated in the Central Vertical Stringer of the Reactor at full power

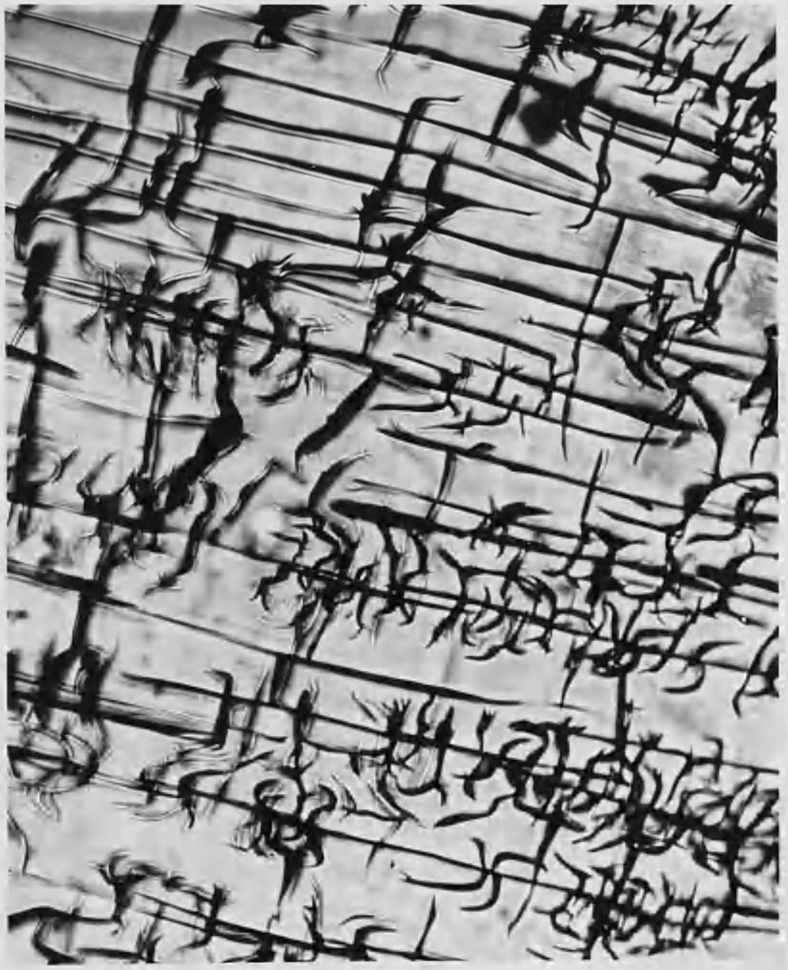


PLATE 3,9

for one hour; Drikold had been packed round the charcoal charges only, so as to further encourage de-gassing of the films. They were next day inserted into two new irradiation vessels, along with an I^{131}-labelled potassium iodide crystal in each case and a new charge of activated charcoal, and once more evacuated with cooling, whilst the activated charcoal was baked out for a further two days. The vessels were sealed off, and irradiated for 15 minutes in the Central Vertical Stringer at full power, <u>completely</u> surrounded by Drikold.

In spite of the above extensive pre-treatment, the gamma-ray spectra were still distorted to a greater extent than that shown in Figure 3,15, but to a considerably less extent than normally observed for films which had received no prior de-gassing. Their autoradiographs were more encouraging than that shown in Plate 3,6 but did not yield such a broad uniform band as in Plate 3,4[1].

This experiment was thus not sufficiently conclusive to allow us to prove that de-gassing of collector films during irradiation was the reason for our inability so far to observe any pattern effect, and indeed it induced us to abandon pre-irradiation de-gassing attempts.

From the observations made so far, the development of collector films which would exhibit no interfering de-gassing tendencies during irradiation seemed desirable. These should yield undistorted spectra.

3.16. Metallic Films As Iodine Collectors

The Collector films used were

(a) Pure Copper Foil (0.001" thick)

and

(b) A sheet of this copper foil covered with a thin layer of palladium, which was deposited at 20°C in the apparatus shown in Figure 3,7.

A sample of each was incorporated into an irradiation system (Figure 3,9), along with activated charcoal and an I^{131}-labelled potassium iodide crystal. During the pre-irradiation bake-out, however, the charcoal was heated in vacuo for two days at a rather higher temperature than usual, viz. 220°C, and in this case, for the first time, the collector films were not cooled during this period. They were then irradiated for 5 minutes at full power in the Central Vertical Stringer. It required an intervening period of 11 days after irradiation to allow the induced radioactivity in the copper to decay, after which it was observed that:-

(i) The spectra of both collector films were entirely undistorted, in agreement with our predictions, and the yields were very high, particularly in the case of the palladium-covered copper, (perhaps due to the higher bake-out temperature).

but

(ii) The recoiled iodine was scattered uniformly over the entire surfaces of both collectors, as shown by autoradiography.

The experiment was repeated, taking the following precautions:

(a) The palladium was deposited on copper with the apparatus surrounded by ice-water.

(b) The pre-irradiation bake-out of the activated charcoal was conducted at a lower temperature (120°C), during which time the collector films were protected by cooling coils.

It was found, 11 days after irradiation, that the spectra were again undistorted, but that the yields were smaller. The autoradiographs showed evidence of a band of recoiled material, Plate 3,10. In this irradiation system, the bottom of the crystal was level with the bottom of the collector, thus accounting for the low horizontal band. On insertion of the palladium-copper collector into the silica tube prior to irradiation, its palladium surface had tended to become slightly scratched towards one side, causing an effective increase in the surface area of palladium at these scratches; this explains why iodine had tended to gather there, as shown in the autoradiograph. This observation provides a rather striking example of the potential surface mobility of iodine on such metallic collectors, which were therefore abandoned in favour of those to be described below.

3.17. The Activated Charcoal-Glass Fibre Collector Films

The possibility of mounting activated charcoal in the form of collector films was investigated, when it was found that charcoal-impregnated glass fibre filter papers had been developed at A.E.R.E., Harwell(3,9) for sampling iodine-bearing vapours, and were commercially available as Whatman ACG/B circular discs of 6 ins. diameter. A piece of this was activated by heating in vacuo at 350°C for 12 hours (when a dark red liquid was given off), then irradiated in the Central Vertical Stringer for 5 minutes at full power. It was found to exhibit a considerable induced activity, from sodium, but this disappeared after 8 days.

Silica vessels of the type shown in Figure 2,2 were employed, although they were of rather larger diameter than the one illustrated, to take account of the thicker nature of these collector films, and to improve their resolution. A charcoal sorption pump was deliberately not incorporated, since it was feared that its sorption influence could induce migration of iodine

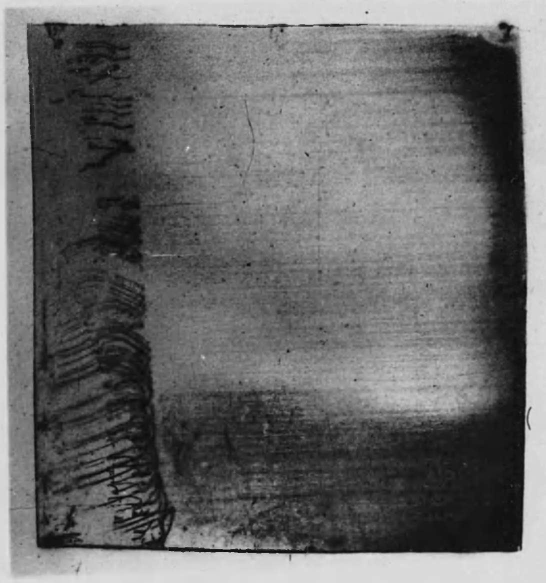


PLATE 3,IO

across the collector.

Two of these previously-de-gassed collector films were each incorporated into a silica vessel along with an I^{131}-labelled potassium iodide crystal. A furnace was fitted over each tube, and the whole system was baked out at 300°C for two days, after which it was irradiated for 5 minutes in the Central Vertical Stringer of the Reactor, at full power.

Seven days later, examination of the collector films in the scintillation counter showed that

(a) The yields were very high (of the same order as had been observed in the first experiment incorporating a palladium/copper collector).

(b) The spectra were perfectly undistorted

but

(c) The iodine was uniformly distributed over the entire collector film, as shown by autoradiography and scintillation scanning.

A repetition of this experiment, in which the irradiation was conducted for one hour in the Thermal Column, resulted in no improvement in the autoradiographs. (Plate 3,11)

Thus again, we had an efficient collector which yielded an undistorted spectrum, but which seemed to be incapable of "holding" the recoiled iodine and preventing subsequent mobility.

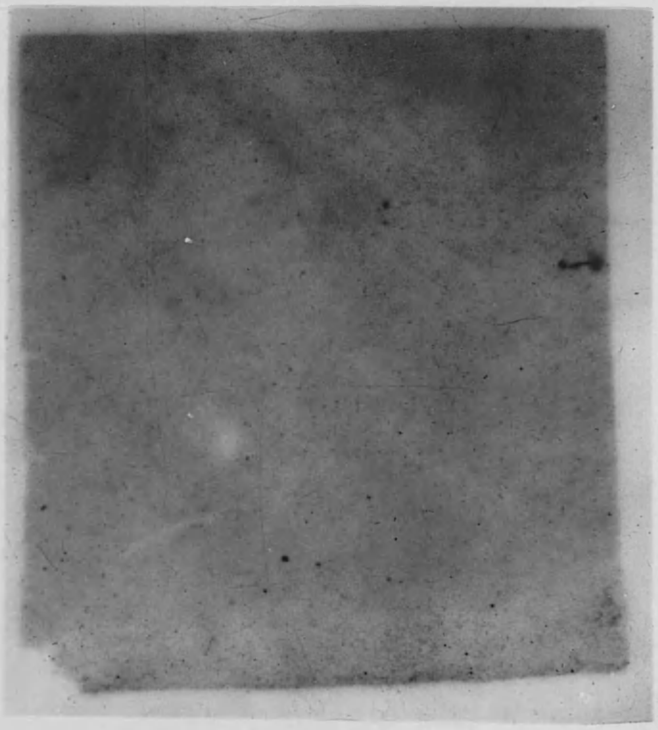


PLATE 3,11

It was decided to use the efficient collecting property of activated charcoal, and its resultant undistorted I^{131} spectrum, to place our observations on a quantitative basis. For this purpose, an improved activated charcoal collector was developed.

3.18. The Aluminium-Activated Charcoal Collector Films

The Whatman collector films described above suffered from two serious disadvantages:

(a) After bake-out and irradiation, they had lost most of their mechanical strength; thus, on attempting to remove them from the tubes, they were very liable to disintegrate.

(b) Their high induced radioactivity meant inconvenient delays between irradiation and subsequent examination.

These difficulties were both overcome by employing collector films consisting of pure aluminium covered by activated charcoal. Their method of preparation, due to Eggleton(3,10) was as follows: a very dilute solution of sodium silicate was spread by means of a camel-hair brush on to a sheet of pure aluminium, and left until it had become tacky; finely-powdered activated charcoal was sprinkled on, and the film baked out in vacuo. Such films showed virtually no induced radioactivity when examined only three days after a 5 minute irradiation in the Central Vertical Stringer.

Since the results from these experiments were required for quantitative calculations, the following precautions were taken:

(i) The irradiations were conducted in the Thermal Column, using the apparatus shown in Figure 3,13. However, in this case, the Polythene box was slid in sideways, so that, in spite of the rapid variation in neutron flux along the length of the Column, each tube would receive a uniform irradiation. In addition, the thermal neutron flux received by each tube was monitored by the use of gold foils, as was the gamma flux by means of Perspex dosimeters (to be described later).

(ii) During the pre-irradiation bake-out, each furnace surrounded the collector film and crystal; this resulted in the silica being more thoroughly de-gassed than in most of the other irradiations. In addition, it did perhaps induce some annealing of the crystal, with an improvement in the perfection of the surfaces.

(iii) These collector films were positioned in the relatively large silica tubes in such a way as to extend above and below the crystal, so as to be sure of collecting all of the recoiled iodine.

On examination of the films three days after irradiation, they showed much the same results as are recorded in the previous section, viz., high yields, undistorted spectra, and a uniform distribution of iodine over their entire surfaces.

The quantitative data obtained from their use will be employed in the following section.

3.18. (A) A Series of Quantitative Experiments Designed to Establish The Precise Amounts of Iodine Recoiled From Potassium Iodide Single Crystals On Neutron Irradiation

The purpose of this section is to calculate the number of iodine atoms which, on average, are recoiled from the potassium iodide crystal surface per (n,γ) event. In order to do so, it is necessary to estimate:-

(a) The ratio of I^{127} to I^{131} atoms on the surface of the crystal before neutron irradiation.

(b) The amount of I^{131} on the surface of the crystal before neutron irradiation.

(c) The amount of I^{131} thrown on to the collector film as a result of neutron irradiation of the labelled potassium iodide crystal.

(d) The total number of (n,γ) events to which the crystal is subjected during neutron irradiation.

In this calculation we shall make use of the results obtained from the experiment described in the previous section; the crystal will be referred to as Crystal 'X' and the aluminium/charcoal collector film as Film 'X'.

In addition, we made use of two standardised I^{131} solutions, obtained from the Radiochemical Centre, Amersham (Catalogue Code No. IBS.1) Their activities were

$$\left.\begin{array}{ll}\text{'A'} & 73.2\ \text{uc.}\\ \text{'B'} & 72.2\ \text{uc.}\end{array}\right\}\ \text{of}\ I^{131}\ \text{at 1348 hours G.M.T. on 21.6.65.}$$

All of the results quoted here are based on these standards, but it should be noted that the methods were developed and the reproducibility of the results checked by the use of Standard I^{131} obtained from the Physics Department of the Western Regional Hospital Board, Glasgow.

(a) To Calculate the Ratio of I^{127} Atoms to I^{131} Atoms on the Surface of Crystal 'X'

We normally used, in the surface exchange labelling technique, 2 mc. of I^{131}, which is incorporated in PdI_2(0.483 gm). If we assume that the latter compound is totally decomposed at the reaction temperature, and that the iodine is condensed on to the surface of the crystal, we may proceed as follows:

$$\underset{360.4\ \text{gm.}}{PdI_2} \longrightarrow Pd + \underset{254\ \text{gm.}}{I_2}$$

Thus 0.483 gm. PdI_2 yields $\frac{254 \times 0.483}{360.4}$ gm I_2

$$= \underline{0.34\ \text{gm. iodine}}$$

The number (N) of I^{131} atoms present in 2 mc. may be calculated using the equation

$A = \lambda N$ where A = Activity (disintegrations/sec.)

and λ = The Disintegration Constant $= \dfrac{0.693}{t_{\frac{1}{2}}}$

$$\therefore N = \frac{A}{\lambda} = \frac{2 \times 3.7 \times 10^{7} \times 8.06 \times 24 \times 60 \times 60}{0.693}$$

$$= \underline{7.38 \times 10^{13}}$$

But the total number of iodine molecules present in 0.34 gm. iodine is

$$\frac{0.34 \times 6.02 \times 10^{23}}{2 \times 127}$$

$$= \underline{8.07 \times 10^{20}}$$

The number of I^{131} atoms is so small that in the molecular state, every I^{131} atom would be in combination with an I^{127} atom, forming an I^{127}-I^{131} molecule. The ratio of these molecules to the inactive I^{127}-I^{127} molecules will be,

$$1 : 1.1 \times 10^{7}$$

The surface exchange reaction may be envisaged as follows:

$$I^{127} - I^{131} + KI^{127} \xrightarrow[\text{Surf.}]{} KI_{3}^{*} \left. \begin{array}{l} \nearrow KI^{131} + I^{127} - I^{127}\ \text{Surf.} \\ \rightarrow KI^{127} + I^{131} - I^{127}\ \text{Surf.} \\ \searrow \underset{\text{Surf.}}{KI^{127}} + I^{131} - I^{127} \end{array} \right.$$

There is only a 1 in 3 chance of an I^{131} atom becoming part of the crystal surface for every exchange taking place between an inactive iodine atom on the surface and a potentially active iodine molecule.

We may conclude that immediately after the exchange reaction,

Ratio of I^{127} atoms to I^{131} atoms on surface of crystal

$$= \underline{3 \times 1.1 \times 10^{7}} \quad ....(1)$$

N.B. It should be noted that the above argument depends on the crystal being completely covered with iodine vapour during the exchange reaction, and on the number of iodine molecules condensed on the crystal surface being very much larger than the number of exchange sites available on the surface. The first of these conditions is experimentally observable, whilst the second will be justified in the subsequent calculation.

(b) <u>To Calculate the Activity of I^{131} on the Surface of Crystal 'X' Immediately after Labelling</u>

<u>Method 1</u>

Average Surface Count of Crystal 'X' 8 days After Labelling = 10,000 d.p.m.
(as recorded by end-window G.M. tube)

Average Surface Count of Crystal 'X' Immediately After Labelling = A_o

where $A_o = A.e^{\lambda t}$ $\qquad \lambda = \frac{0.693}{8.06}$, t = 8 days

$$\therefore A_o = 10,000 \times 2.00$$

$$= \underline{20,000 \text{ d.p.m.}}$$

Method

A reference crystal of potassium iodide (40 x 5 x 5m was cleaved, polished, and annealed in the usual way, then labelled with I^{131} by the surface exchange method:-

Average Surface Count of Reference Crystal Immediately After Labelling = 46,494 d.p.m.

This crystal was dissolved in water, transferred to a 100 ml standard flask, and the solution made up to the mark with water. 5 ml of this diluted solution was then pipetted via a safety pipette, into a Pyrex centrifuge tube, to which was added, via a filter, palladium chloride (235 mg.), dissolved in dilute sodium chloride solution. The whole was heated to boiling for a few minutes to coagulate the precipitated palladium iodide, which, on removal of the supernatant water by centrifugation, was washed several times with methanol. It was transferred as a methanol slurry to an aluminium planchette, and dried under an infra-red lamp. The palladium iodide (170 mg.) was then sealed into a Cellophane packet for subsequent examination in the scintillation counter.

This treatment was repeated for another 5 ml sample of the solution.

The Amersham Standardised I^{131} Solution 'B' was transferred to a litre standard flask with AnalaR potassium iodide (15.65 gm.) and diluted to the mark with water. 10 ml. of this solution were then transferred to a Pyrex centrifuge tube, to which was added palladium chloride (235 gm.). The above treatment was repeated, again yielding palladium iodide (170 mg.).

This procedure was repeated, using another 10 ml. of solution.

These four palladium iodide precipitates were counted next day (1445 hours G.M.T. on 5.7.65) by means of the scintillation counter and Laben pulse height analyser equipment, and their activities compared by integrating the I^{131} 0.364 M.eV. photopeak over 10 channels

Results

	Individual Integrated Count	Average Integrated Count
Reference Crystal	34,508; 34,755	34,632
Standardised I^{131}	48,536; 50,791	49,664

Activity of Amersham Standardised Solution 'B' at 1348 hours G.M.T. on 21.6.65. = 72.2 uc.

Activity (A) on day of counting may be calculated as follows:-

$$A_0 = 72.2 \text{ uc} \qquad t = \frac{336.95}{24} \text{ days} \qquad t_{\frac{1}{2}} = 8.06 \text{ days}$$

$$A = A_0 . \exp(-\lambda t)$$

$$= 72.2 \exp\left(- \frac{0.693 \times 336.95}{24 \times 8.06}\right) \text{uc.}$$

$$= 21.75 \text{ uc.}$$

But the amount of activity on each planchette was 1/100th of activity present in Amersham Solution 'B'

Amount of Activity Present on Planchette = 0.2175 uc.

Thus,

Activity Yielding Count of 49,664 = 0.2175 uc.

" " " " 34,632 = $\frac{0.2175 \times 34{,}632}{49{,}664}$

= 0.1517 uc.

But this figure represents 1/20th of total activity present on surface of crystal.

∴ Total Activity on Surface of Crystal = 0.1517 x 20 uc.

= 3.034 uc

However,

Average Surface Count for Reference Crystal = 46,494

Whereas

Average Surface Count for Crystal 'X' = 20,000

∴ Activity on Surface of Crystal 'X' Immediately

After Labelling = $\frac{20{,}000 \times 3.034}{46{,}494}$

= 1.31 uc. ....(2)

= 4.79×10^{10} atoms I^{131}

Method 2

Amersham Standardised I^{131} solution 'A' was transferred to a 100 ml standard flask with AnalaR potassium iodide (10 mg.) and made up to the mark with water. 20 ml of this solution was then transferred to a Pyrex centrifuge tube, to which was added palladium chloride (19 mg.) in dilute sodium chloride solution. The whole was heated to boiling for a few minutes to coagulate the precipitate, which, on removal of the supernatant water by centrifugation, was washed several times with methanol, being then transferred evenly as a methanol slurry to the four faces of a polished, annealed, potassium iodide single crystal (40 x 5 x 5 mm.) and dried under an infra-red lamp.

This treatment was repeated with another similar single crystal.

Each crystal was counted with an end-window G.M. tube at 1200 hours G.M.T. on 6.7.65.

Results

Mean Surface Activity of First Crystal	=	67,241 d.p.m.
" " " " Second Crystal	=	70,077 d.p.m.
Average Surface Activity	=	68,659 d.p.m.

Activity of Amersham Standardised Solution 'A' at 1348 hours G.M.T. on 21.6.65. = 73.2 uc.

Thus the Activity (A) on the day of counting may be calculated as follows:

$$A_o = 73.2 \text{ uc.} \qquad t = \frac{358.2}{24} \text{ days} \qquad t_{\frac{1}{2}} = 8.06 \text{ days.}$$

$$A = A_o \exp(-\lambda t)$$

$$= 73.2 \exp\left(-\frac{0.693 \times 358.2}{24 \times 8.06}\right) \text{uc.}$$

$$= \underline{19.95 \text{ uc}}.$$

But only one fifth of this amount was transferred to the surface of each crystal

$\therefore$ Activity on Surface of Each Crystal Immediately After Labelling $= \frac{19.95}{5} = 3.99$ uc.

From Above,

Average Surface Count of Crystal = 68,659 d.p.m.

Whereas

Average Surface Count of Crystal 'X' = 20,000 d.p.m.

$\therefore$ Activity on Surface of Crystal 'X' Immediately After Labelling $= \frac{3.99 \times 20{,}000}{68{,}659}$

$= \underline{1.16 \text{ uc}}$.

__N.B__. The answer previously obtained equation (2) shall be used in the remainder of this calculation, since it is the result of a more accurate method.

(c) __To Calculate the Amount of I^{131} Thrown on to Collector Film 'X' as a Result of Neutron Irradiation__

Since, in a typical neutron irradiation, the recoiled iodine atoms are collected by a palladium-polystyrene film in the form of palladium iodide, it was decided to simulate this by spreading a known amount of I^{131} in the form of palladium iodide on to a piece of polystyrene film.

__Method__

Amersham standardised I^{131} Solution 'A' had previously been transferred to a 100 ml standard flask with AnalaR potassium iodide (10 mg.), and diluted to the mark with water. 10 ml of this solution was placed via a safety pipette into a Pyrex centrifuge tube, to which was added palladium chloride (19 mg.) in dilute sodium chloride solution. The whole was heated to boiling for a few minutes to coagulate the precipitate of palladium iodide, which, on removal of the supernatant water by centrifugation, was washed several times with methanol, then transferred (under an infra-red lamp) to the polystyrene film as a band of evenly spread methanol slurry. (The region of the polystyrene used for this purpose had previously been covered with a thin film of soap solution to facilitate even spreading of the slurry).

This procedure was repeated, using another similar film.

An autoradiograph of one of these films is shown in Plate 3,12.

The films were counted on the scintillation counter (1450 hours G.M.T. on 5.7.65) and their activities, obtained by integrating their I^{131} 0.364 M.eV. peaks over 10 channels, were compared with the corresponding activity of Film X.

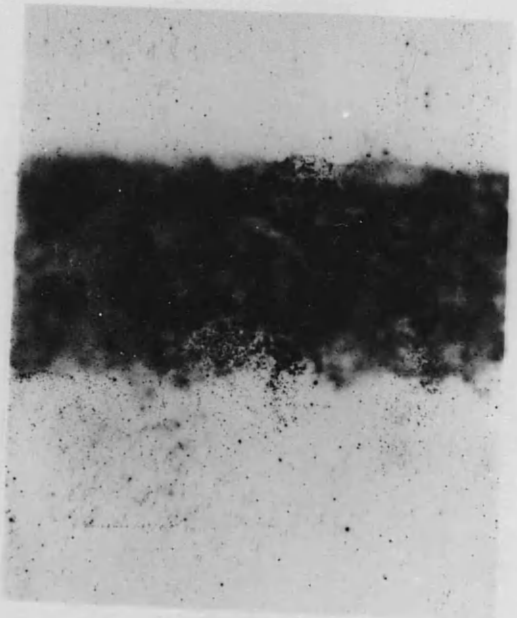


PLATE 3,I2

Results

	Individual Integrated Counts	Average Integrated Count
Films Coated with Standardised I^{131}/PdI_2	368,368; 342,125	355,247
Film 'X'		11,705

Activity of Amersham Standardised I^{131} Solution 'A' at 1348 hours G.M.T. on 21.6.65. = 73.2 uc.

therefore The Activity (A) at the time of counting may be calculated as follows:

$$A_0 = 73.2 \text{ uc.} \qquad t = \frac{337.02}{24} \text{ days} \qquad t_{\frac{1}{2}} = 8.06 \text{ days.}$$

$$A = A_0 \exp(-\lambda t).$$

$$= 73.2 \exp\left(- \frac{0.693 \times 337.02}{8.06 \times 24}\right) \text{uc.}$$

$$= \underline{22.05 \text{ uc}}.$$

But the activity spread on to the surface of each film was one tenth of this.

∴ Activity on Surface of Each Film = 2.205 uc.

From Above,

Activity Represented by Integrated Count of 355,247 = 2.205 u

∴ Activity Represented by Integrated Count of 11,705

$$= \frac{2.205 \times 11,705}{355,247} \text{ uc.}$$

$$= \underline{0.073 \text{ uc}}.$$

But the gamma-ray spectrum of Film 'X' was recorded 67 hours after irradiation.

$\therefore$ The Activity (A_o) on the surface of the film immediately after irradiation is given by

$$A_o = A \exp(\lambda t)$$

$$= 0.073 \exp\left(\frac{0.693 \times 67}{8.06 \times 24}\right) \text{ uc.}$$

$$= \underline{0.093 \text{ uc.}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$= \underline{3.5 \times 10^9 \text{ atoms } I^{131}}$$

(d) <u>To Calculate the Number of (n,γ) Events to which Crystal 'X' was Subjected During Neutron Irradiation</u>

Volume of Crystal = 3.6 x 0.5 x 0.5 cc.

= 0.9 cc.

Density of KI = 3.13 gm/cc.

Wt. of Crystal = 2.82 gm.

$\therefore$ No. of Molecules of KI Present $= \frac{2.82 \times 6.02 \times 10^{23}}{166}$

= No. of Iodine Atoms Present.

Thermal Neutron Flux (Measured by means of gold foils) = 2.12×10^{11} neutrons/cm^2/sec.

Thermal Neutron Cross-Section of I-127 = 6.7 barns.

Duration of Irradiation = 30 x 60 secs.

$\therefore$ Total No. of (n,γ) events:

$$\frac{2.82}{166} \times 6.02 \times 10^{23} \times 6.7 \times 10^{-24} \times 2.12 \times 10^{11} \times 30 \times 60$$

$$= \underline{2.61 \times 10^{13}} \quad \ldots\ldots\ldots\ldots\ldots (4)$$

It has previously been noted equation (1) that the ratio of I^{127} to I^{131} atoms on the crystal surface on the day on which the I^{131} was obtained would be 3.3×10^7.

However, the irradiation of crystal 'X' was performed 8 days after having taken delivery of the I^{131}.

$\therefore$ Ratio of I^{127} to I^{131} Atoms on Crystal Surface on Day of Irradiation = $\underline{6.6 \times 10^7}$

From Equation (3).

Amt. of I^{131} Collected by Film 'X' = 0.093 uc.

= 3.5×10^9 atoms I^{131}

From Above

Total Number of Iodine Atoms Recoiled from Crystal on Irradiation = $3.5 \times 10^9 \times 6.6 \times 10^7$

= $\underline{2.32 \times 10^{17}}$ ....(5)

Thus from Equations (4) and (5)

No. of Iodine Atoms Recoiled per (n,γ) Event = $\dfrac{2.32 \times 10^{17}}{2.6 \times 10^{13}}$

= $\underline{9.0 \times 10^3}$..(

Note

This calculation had initially been performed using the Previously De-gassed Collector Film (Section 3,13) and its associated crystal. It yielded the results:

Activity of Crystal Surface After Labelling = 2.716 uc.

Activity on Collector Film After Irradiation = 0.105 uc.

= 3.9×10^{9} atoms I^{131}

Total No. of Iodine Atoms Recoiled from Crystal on Irradiation = $3.9 \times 10^{9} \times 6.6 \times 10^{7}$

= 2.6×10^{17}

Total No. of (n,γ) Events = 2.69×10^{13}

No. of Iodine Atoms Recoiled per (n,γ) Event

$$= \frac{2.6 \times 10^{17}}{2.69 \times 10^{13}}$$

$$= \underline{9.6 \times 10^{3}}$$

This is in good agreement with Equation (6)

(e) <u>To Calculate the Number of Iodine Atoms on the Surface of Crystal 'X', Assuming the Latter to be Perfectly Smooth</u>

Dimensions of crystal = 36 x 5 x 5 mm.

This crystal was cleaved so as to expose its (100) faces.

Distance Between Iodine Atoms Along Edge of (100) Faces = 7.05 Å

Distance Between Rows of Iodine Atoms Parallel to Such Edges = 3.53 Å

<u>The (5 x 5) mm. Face</u>

Number of Iodine Atoms Along Any Edge $= \frac{5 \times 10^{7}}{7.05}$

Number of Rows of Atoms Parallel to this Edge $= \frac{5 \times 10^{7}}{3.53}$

Number of Iodine Atoms on (5 x 5) mm. Face $= \frac{5 \times 10^{7}}{7.05} \times \frac{5 \times 10^{7}}{3.53}$

The Four (36 x 5) mm. Faces

In a similar manner to the above, it may be shown that

Total Number of Iodine Atoms on the Surface of These Four Faces $= \frac{4 \times 36 \times 10^7}{7.05} \times \frac{5 \times 10^7}{3.53}$

∴ Total Number of Iodine Atoms on the Surfaces of the 5 Faces (the 6th face is stuck on to the silica rod)

$$= \frac{5 \times 10^7}{7.05} \times \frac{5 \times 10^7}{3.53} + \frac{4 \times 36 \times 10^7}{7.05} \times \frac{5 \times 10^7}{3.53}$$

$$= \underline{2.99 \times 10^{15}} \quad \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

It has already been shown that the ratio of I^{127} atoms to I^{131} atoms on the surface of the crystal is $3 \times 1.1 \times 10^7$.

This assumes, however, that the exchange reaction would be performed on the day on which the 2 mc. of I^{131} was obtained, which is not practicable. In fact, the exchange reaction on Crystal 'X' was performed four days after taking delivery of the I^{131}; therefore, since the half-life of I^{131} is 8 days,

Ratio of I^{127} Atoms to I^{131} Atoms on Surface of Crystal Immediately After Exchange $= 4.5 \times 1.1 \times 10^7$

But it has already been shown (Equation (2)) that Number of I^{131} Atoms on Surface of Crystal 'X' Immediately After Exchange $= 4.79 \times 10^{10}$

$$\therefore \frac{\text{No. of } I^{127} \text{ Atoms on Surface of Crystal 'X' (Observed)}}{\text{No. of } I^{127} \text{ Atoms on Surface of Crystal 'X' (Calculated)}}$$

$$= \frac{4.79 \times 10^{10} \times 4.5 \times 1.1 \times 10^{7}}{2.99 \times 10^{15}}$$

$$= \underline{7.93 \times 10^{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

This is a measure of the extent to which the crystal surface departs from ideality. It will be referred to as the Surface Roughness Factor of Crystal 'X' and will subsequently be invoked in a discussion of the reasons for the high yields of iodine recoiled per (n,γ) event.

3.19 The Gamma-Ray Irradiations

It was necessary to clarify the contribution made to our previous observations by the Reactor gamma-ray flux, since it was suspected that gamma irradiation could contribute to the yield of iodine recoiled from the crystals for the following reasons:

(a) Kazanjian and Libby have shown (3,11) that in n-propyl bromide, similar hot atom processes occur whether the bromine recoils due to an (n,γ) reaction or, in decaying from the Br^{80m} to the ground state, produces Auger electrons, thus leaving it with a positive charge, which causes disruption of the C-Br bond. The result of this process is an explosion of the molecule, thus producing a bromine atom which behaves like one produced via an (n,γ) reaction.

An Auger vacancy cascade can be created in an iodine atom by X-ray bombardment, and the chemical consequences would be the same as if the iodine had undergone internal conversion.

(b) Iyer and Willard have recently stated (3,12) that essentially all of the yields and products distributions which have been reported for chemical activation via radioactive neutron capture by Br^{81} have been due to isomeric transition of the short-lived Br^{82m} and not due to a simple (n,γ) process.

(c) G.N. Walton (3,13) has pointed out that some features of the present position on theories of the chemical effects of nuclear transformation are unsatisfactory; he suggests that theories based exclusively on the transfer of energy by elastic collisions of recoiling atoms are inadequate to explain all of the experimental observations. Instead, electronic excitation and consequent loss of valency bonding could be of great importance. In contrast, direct transfers of photon energy to the nucleus via either a direct Compton event or a photonuclear reaction are too small to contribute; indeed, the second mode is of little importance even for those nuclei susceptible to (γ, n) reactions, for energies below 10 M.eV.(1,16).

It was thus decided to irradiate an I^{131}-labelled potassium iodide crystal in a flux of gamma-radiation, using the activated charcoal/Drikold system (Fig. 3,9). A palladium/polystyrene collector film was chosen because

(i) most of our observations to date had utilised these

and

(ii) it offered an opportunity to observe any possible distortion in the spectrum of recoiled I^{131} in a neutron-free environment.

The Irradiation Source

The gammairradiations were conducted at the plant of Ethicon Ltd., Edinburgh. This has an initial loading of 40,000 Curies of Cobalt-60 and incorporates an irradiation conveyer in which the materials being irradiated are in continuous movement around the source, as shown diagramatically in Plate 3,13. The irradiation tubes were packed into a large Polythene bottle with Drikold, then placed in one of the aluminium containers which was loaded automatically from the storage rollerveyors E to F, and transported into the Co^{60} cell, where it was lifted from G to a position alongside D. From there it was subjected to the illustrated radiation cycle, in which it passed the fuel elements four times, thus ensuring uniform irradiation, over a period of 40 hours. It was then transferred from the elevator at D to the conveyor at A, thence back to the conveyor rolling room, where it passed from B to the storage rollerveyor at C.

The total gamma dose received by the samples was 2.9 M.rads. This is higher than the gamma dose which would be received by a sample irradiated at full power in the Central Vertical Stringer of the Reactor (estimated to be 2.5 M.rads).

It should be noted that the Cobalt-60 Source emits gamma radiation in two discrete quanta of energy,

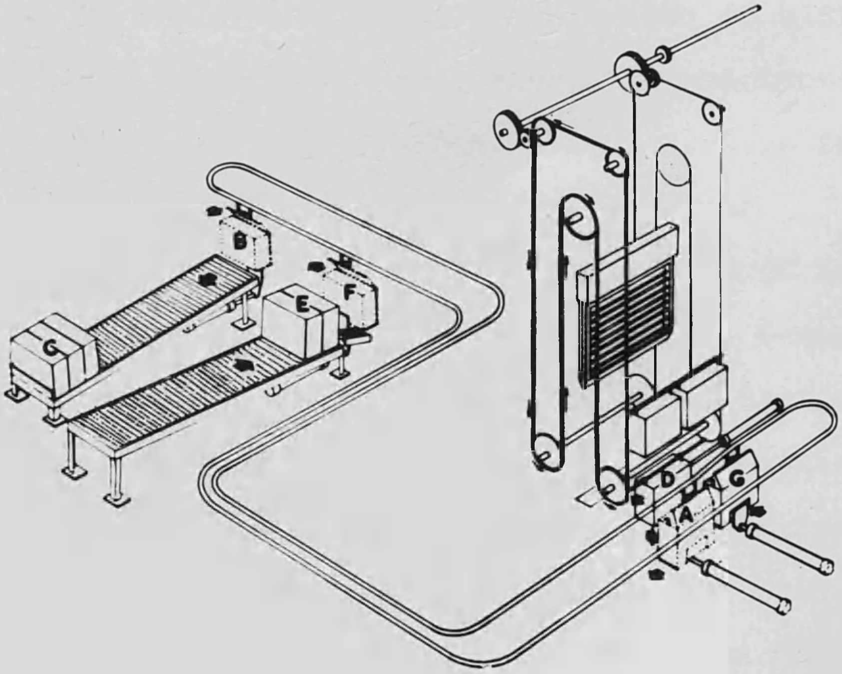


PLATE 3,I3

viz., 1.17 and 1.33 M.eV., whereas the Reactor gamma energies vary between wide limits. However, for our purposes, the intensities of the two sources can be compared by their relative abilities to generate colour centres in potassium iodide, since, as will be discussed later, colour centres are an integral part of the mechanism by which iodine is ultimately recoiled from potassium iodide on gamma irradiation.

On examination of the collector films in the scintillation counter, it was found that

(a) The amount of I^{131} collected was of the same order as would be collected during a 5 minute irradiation in the Central Vertical Stringer. This observation, taken in conjunction with the cadmium-shielded irradiations, proved that thermal neutrons were mainly responsible for the previous observations but that gamma radiation can initiate recoils to a significant extent. The mechanism by which this can take place will be discussed in detail later.

(b) The I^{131} gamma-ray spectrum of the collector film was entirely undistorted,

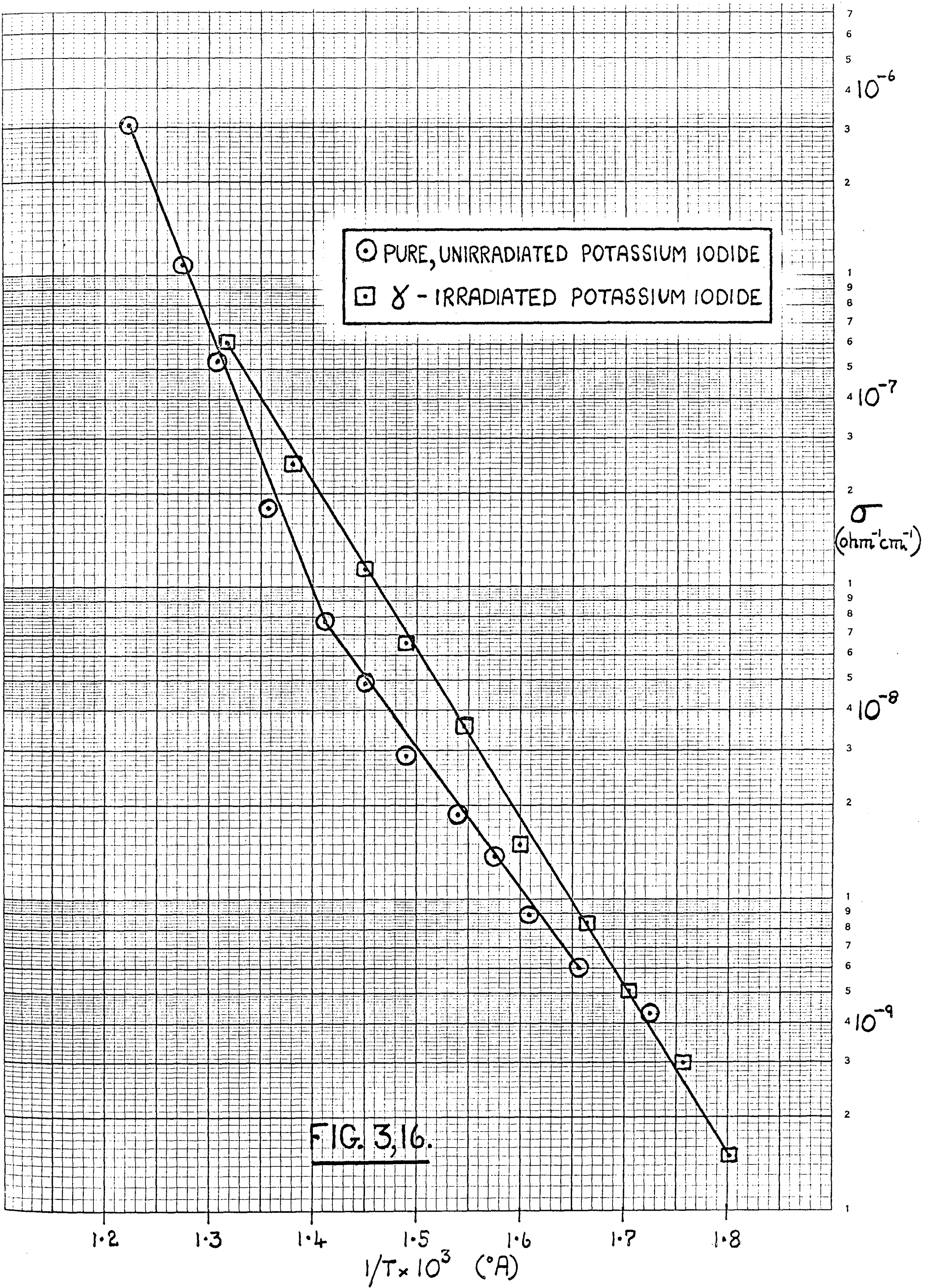
but

(c) The I^{131} gamma-ray spectrum of the charcoal sorption pump was fairly distorted when recorded three days after irradiation: the peak at 0.28 M.eV.

was almost as high as that at 0.364 M.eV.

Ionic conductivity measurements were made on a sample of this crystal, and compared with a similar crystal of pure, unirradiated potassium iodide. The result is shown in Fig. 3,16 and will be considered later.

The crystals used in this irradiation were found to have become bright green due to the presence of F-Centres. Since the generation of these colour centres is an integral part of the mechanism by which gamma-irradiation can initiate focused collision sequences in potassium iodide, confirmation of their presence was sought by subjecting the crystals to electron spin resonance examination at room temperature four days after the irradiation. By this time, however, the crystals had turned brown, due, it was thought, to bleaching of the F-centres by light, and exhibited no paramagnetism. For this reason, a gamma irradiation was performed once more at the Ethicon plant, using irradiation tubes which had been painted black. After irradiation, the crystals were stored in a black bottle in Drikold. On subsequent electron spin resonance examination at room temperature, they again failed to show a paramagnetic signal, although they were still green.



⊙ PURE, UNIRRADIATED POTASSIUM IODIDE
⊡ γ - IRRADIATED POTASSIUM IODIDE
10^{-6}
10^{-7}
10^{-8}
10^{-9}
σ
(ohm⁻¹cm⁻¹)
1·2
1·3
1·4
1·5
1·6
1·7
1·8
1/T × 10³ (°A)

FIG. 3,16.

3.20. Dosimetry and Colour Centres

The thermal neutron doses received by the samples on Reactor neutron irradiation were routinely measured by incorporating into each irradiation bottle a pair of gold foils of approximately 40 mg. weight, which were counted three weeks later in a callibrated arrangement on the scintillation counter. The thermal neutron flux could then be calculated by the use of an appropriate correction factor (see Appendix).

In the Ethicon irradiations, the gamma-ray flux was measured by means of 1 mm. thick clear Perspex strips, (3,14) cut to size so as to fit into the cell holder of a Unicam 500 U.V. Spectrophotometer. Doses of gamma radiation up to 3 M.rad. increase the optical density at 292 m.u. in an almost linear manner. Thus immediately after irradiation, the optical density of each strip was compared with a standard. Having measured its thickness with a micrometer, the dose which it had received was obtained by reference to a callibration table (Table 3) supplied by U.K.A.E.A., Wantage. By this method, it is possible to measure accurately a gamma-ray dose between the limits 1.5 M.rad. and 3.5 M.rad.

During Reactor irradiation in the Central Vertical Stringer, the samples were exposed to a mixed flux of thermal neutrons, gamma-rays, and fast neutrons. It is extremely difficult to monitor each of these

TABLE 3

Relationship Between Optical Density Difference per Unit Thickness (ΔK) and Dose
(Unit Thickness = 1")

ΔK	Dose	ΔK	Dose	ΔK	Dose
175·8	2·25	194·9	2·51	213·8	2·77
176·6	2·26	195·6	2·52	214·5	2·78
177·4	2·27	196·3	2·53	215·2	2·79
178·2	2·28	197·0	2·54	215·9	2·80
179·0	2·29	197·6	2·55	216·7	2·81
179·8	2·30	198·4	2·56	217·4	2·82
180·5	2·31	199·1	2·57	218·1	2·83
181·2	2·32	199·8	2·58	218·9	2·84
181·9	2·33	200·6	2·59	219·7	2·85
182·6	2·34	201·4	2·60	220·6	2·86
183·4	2·35	202·1	2·61	221·3	2·87
184·1	2·36	202·8	2·62	222·0	2·88
184·8	2·37	203·5	2·63	222·7	2·89
185·5	2·38	204·2	2·64	223·5	2·90
186·2	2·39	205·0	2·65	224·2	2·91
186·9	2·40	205·8	2·66	224·9	2·92
187·7	2·41	206·5	2·67	225·6	2·93
188·5	2·42	207·2	2·68	226·4	2·94
189·3	2·43	208·0	2·69	227·1	2·95
190·1	2·44	208·8	2·70	227·8	2·96
190·8	2·45	209·6	2·71	228·4	2·97
191·5	2·46	210·3	2·72	229·0	2·98
192·2	2·47	211·0	2·73	229·7	2·99
192·9	2·48	211·8	2·74	230·4	3·00
193·6	2·49	212·6	2·75	231·1	3·01
194·3	2·50	213·2	2·76	231·8	3·02

components in the presence of the others. However, we were able to clarify the situation by making use of the generation of colour centres under certain conditions. Previous irradiations performed in the Central Vertical Stringer (using the simple apparatus shown in Fig. 2,2) produced a bright green colour in the potassium iodide crystals, which, on being removed from the tubes, turned brown within a few hours; the silica tubes became violet in colour. On the other hand, irradiations performed in the Thermal Column with the same system yielded colourless crystals and tubes. When the improved irradiation apparatus (Fig. 3,9) was used, surrounded by Drikold, both the crystals and the silica tubes remained almost colourless even after irradiation for one hour at full power in the Central Vertical Stringer. Thermal neutron flux measurement proved that the Drikold had thermalised the fast neutron flux by 24%, viz.

Without Drikold

Thermal Neutron Flux = $1.09 \times 10^{12} n/cm^2/sec.$

Fast Neutron Flux = $3.73 \times 10^{11} n/cm^2/sec.$

With Drikold

Thermal Neutron Flux = $1.18 \times 10^{12} n/cm^2/sec.$

Extra No. of Thermal Neutrons Produced, Due to Presence of Drikold = $9.0 \times 10^{10} n/cm^2/sec.$

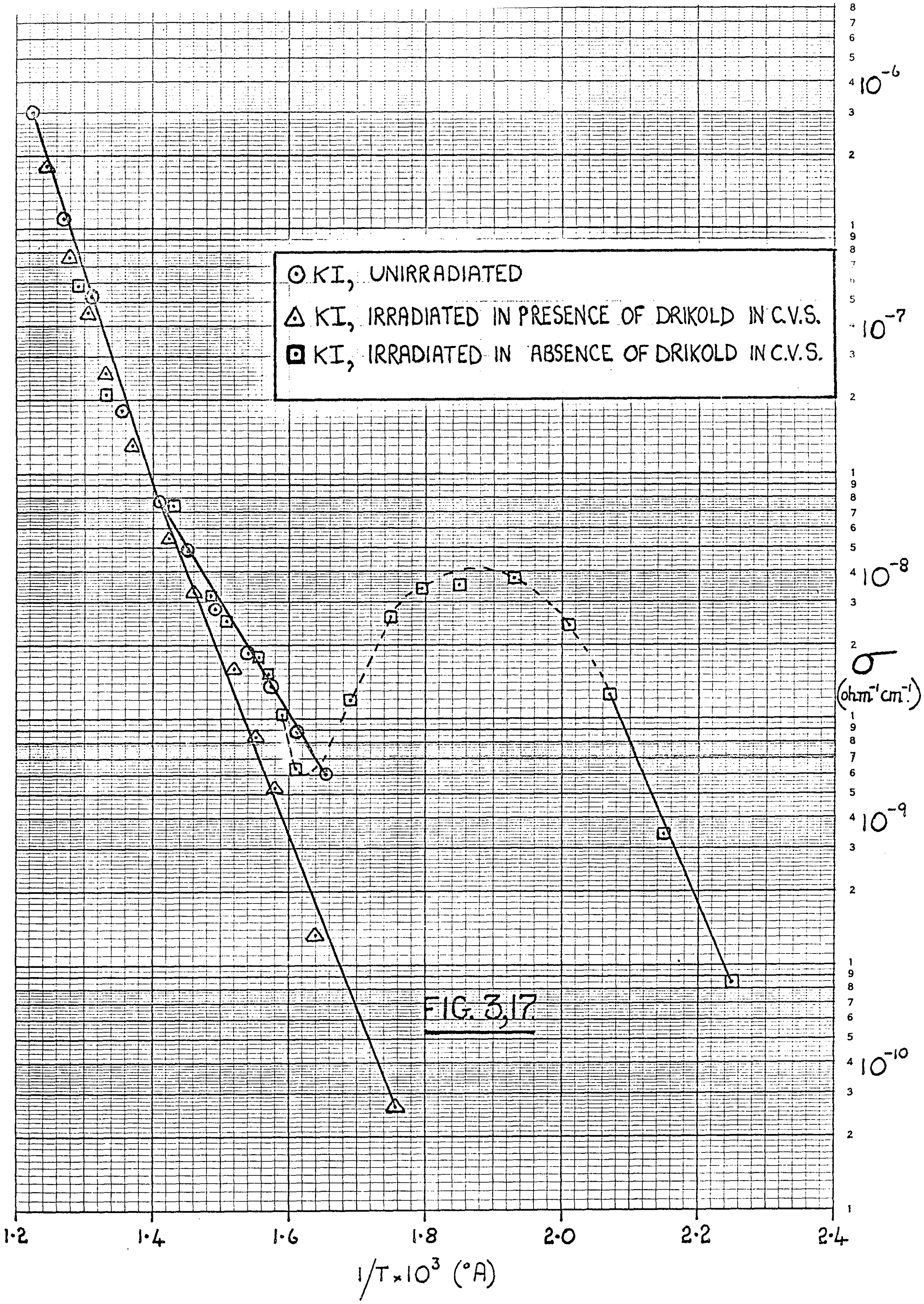
$\therefore$ % Thermalisation of Fast Neutron Flux $= \dfrac{9.0 \times 10^{10}}{3.73 \times 10^{11}} \times 100$

= 24.3%

Thus it appeared that the generation of colour centres on Reactor irradiation was caused by fast neutrons. This was confirmed by performing a comparative ionic conductivity experiment on a crystal which had been irradiated in the Central Vertical Stringer in the absence of Drikold with one which had been surrounded by Drikold (Fig. 3,17); the former shows evidence of considerable radiation damage.

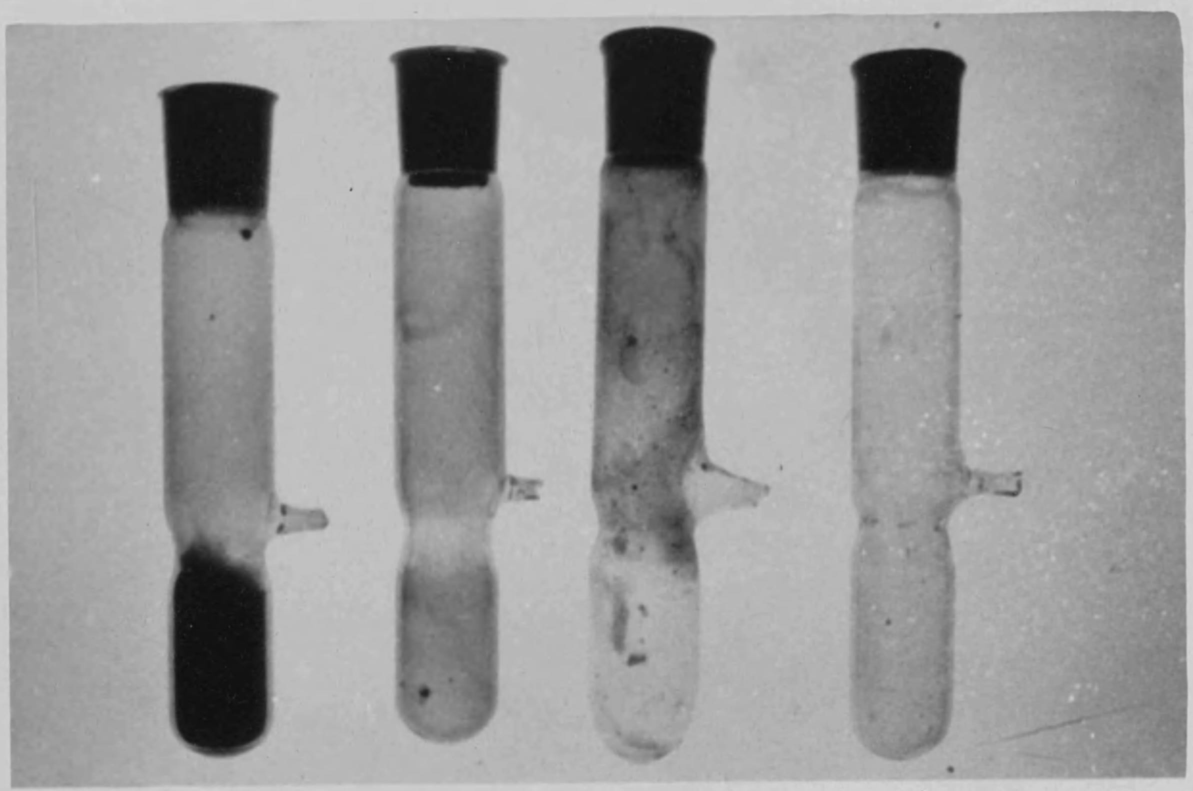
Further proof of these conclusions may be deduced from Plate 3,14, which shows a selection of silica irradiation tubes. Tubes (A) and (B) were irradiated in a gamma-ray flux by Ethicon Ltd., after which the charcoal was removed from (B) to reveal that the colour centres extended to the bottom of the tube. Tube (C) was irradiated in the Central Vertical Stringer; it may be seen how the charcoal charge which was present during irradiation has thermalised the fast neutron flux sufficiently to reduce colour centre formation in its immediate vicinity. Tube D was irradiated in the Central Vertical Stringer in the absence of any charcoal, but surrounded by Drikold.

These observations lead to the conclusion that Reactor gamma-rays are of little importance in our observations; indeed Perspex dosimeters incorporated in the Thermal Column irradiations in Drikold showed virtually no change in optical density (ΔK was < 1).



⊙ KI, UNIRRADIATED
△ KI, IRRADIATED IN PRESENCE OF DRIKOLD IN C.V.S.
▣ KI, IRRADIATED IN ABSENCE OF DRIKOLD IN C.V.S.
10⁻⁶
10⁻⁷
10⁻⁸
10⁻⁹
10⁻¹⁰
σ (ohm⁻¹ cm⁻¹)
1·2
1·4
1·6
1·8
2·0
2·2
2·4
1/T × 10³ (°A)

FIG. 3.17



(A) (B) (C) (D)

PLATE 3,14

3.21. Experiments Designed to Clarify The Nature of the Distorted Spectra

The preliminary observations described earlier had established that distortion of the I^{131} spectra, which had been observed with de-gassing collector films, was not caused by impurities in the crystals, collectors, or charcoal sorption pump. It was initially postulated that the large peak at 0.16 M.eV. was due to Xe^{131m}, which should therefore have been removable by heating in vacuo, leaving the iodine (represented by the 0.364 M.eV. peak) on the film as palladium iodide. Two palladium-covered polystyrene films showing distorted spectra were used for this purpose; one (Film 'A') was heated at 67°C in vacuo for 22 hours, whilst the other was retained for comparison.

Integrated Peak Areas

	Film 'A'			Film 'B'		
	0.16	0.28	0.364 M.eV.	0.16	0.28	0.364 M.eV.
Before Heating	7,241	47,594	5,293	3,089	14,966	4,265
After Heating	2,960	20,170	4,322	2,246	13,601	3,482
Fall in Activity	59.1%	52.62%	18.3%	27.3%	9.2%	18.3%

Thus, the species responsible for the activity at 0.16 M.eV. was removable on heating as predicted, but so was that at 0.28 M.eV. (The presence of an enhanced peak at 0.08 M.eV. became apparent later).

It was therefore decided to utilise the volatility of these extra components to separate them from the pure I^{131}. An irradiation was performed in the usual way (Fig. 3,9) in the Central Vertical Stringer, in Drikold, for one hour at full power, using palladium-polystyrene collector films which had not been previously de-gassed. Three days later, the collector films (hereafter referred to as 'A' and 'B') and their associated charcoal sorption pumps were examined in the scintillation counter. The charcoal pumps were too radioactive, particularly due to a very large peak at 0.08 M.eV., to allow satisfactory spectra to be recorded. Five days after the irradiation, Film A was placed in the stoppered tube of the apparatus shown in Fig. 3,18 and the system evacuated through taps C,D and E for a few minutes, after which tap C was closed. The charges of activated charcoal in U-tubes P and Q were then de-gassed at 350°C until the vacuum in the system, as measured on a McLeod gauge, was 10^{-4} Torr. The furnaces were removed, tap E immediately closed, the charcoal allowed to cool, and U-tube Q immersed in liquid nitrogen. Tap B was then opened momentarily and closed again, to allow a

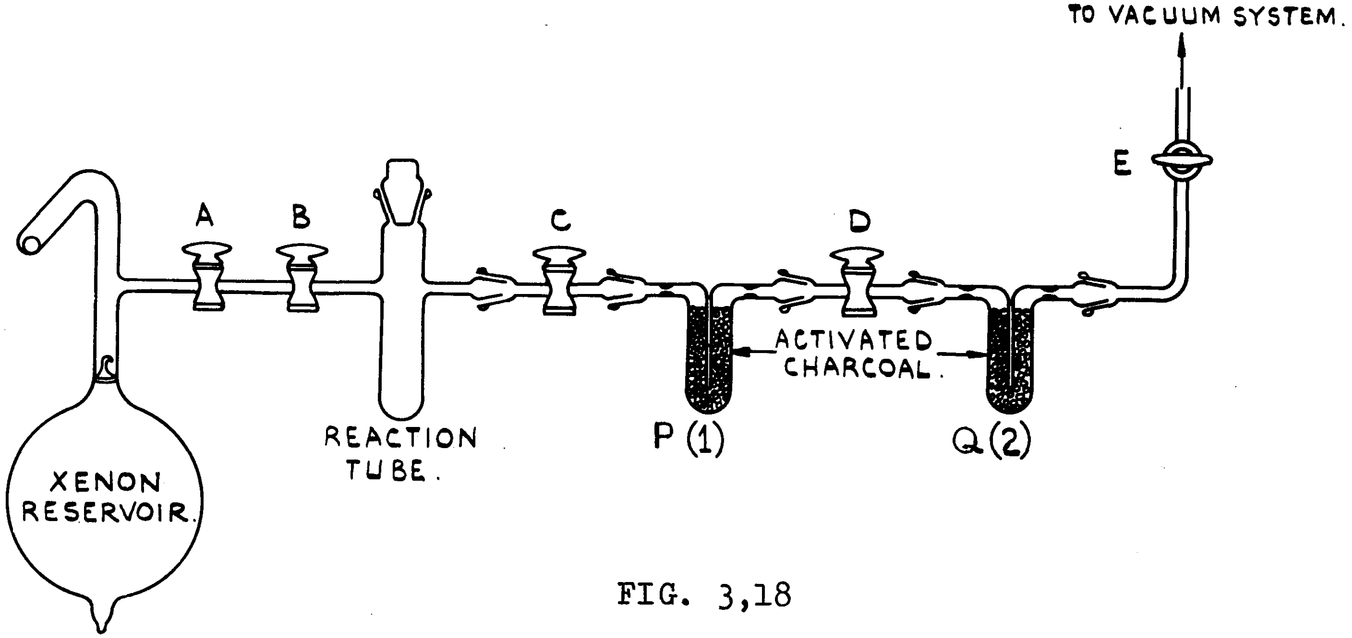

TO VACUUM SYSTEM.
E
A
B
C
D
XENON RESERVOIR.
REACTION TUBE.
ACTIVATED CHARCOAL.
P (1)
Q (2)

FIG. 3,18

charge of inactive xenon carrier gas to enter the tube holding Film A, which was heated at 85°C for 5 minutes. After this, tap C was opened, and the heating continued for a further 30 minutes. U-tubes P and Q were then sealed off and removed from the system for examination in the scintillation counter. (Their dimensions had been so chosen as to allow them to sit neatly on top of the crystal, thus ensuring reproducible counting geometry). U-tube P had been designed to collect any iodine which may have been realeased on heating the film, allowing the more volatile products to be condensed into U-tube Q. It was found, however, that it was P which collected the volatile products, with peaks at 0.08, 0.16 and 0.28 M.eV., whilst Q collected almost pure I^{131}: their spectra, recorded 7 days after the separation, are shown in Fig. 3,19. A more meaningful method of comparison is shown in Figs. 3,20 (U-tube P) and 3,21 (U-tube Q), which compare the decay rates of the various peaks. (Note: in computing the peaks, each was integrated over 5 channels and corrected for neighbouring peak influence by subtracting from the average integrated count the mean trough on either side). Fig. 3,21 proves that considerable separation was achieved; the decay rates are surprisingly close to pure I^{131}:

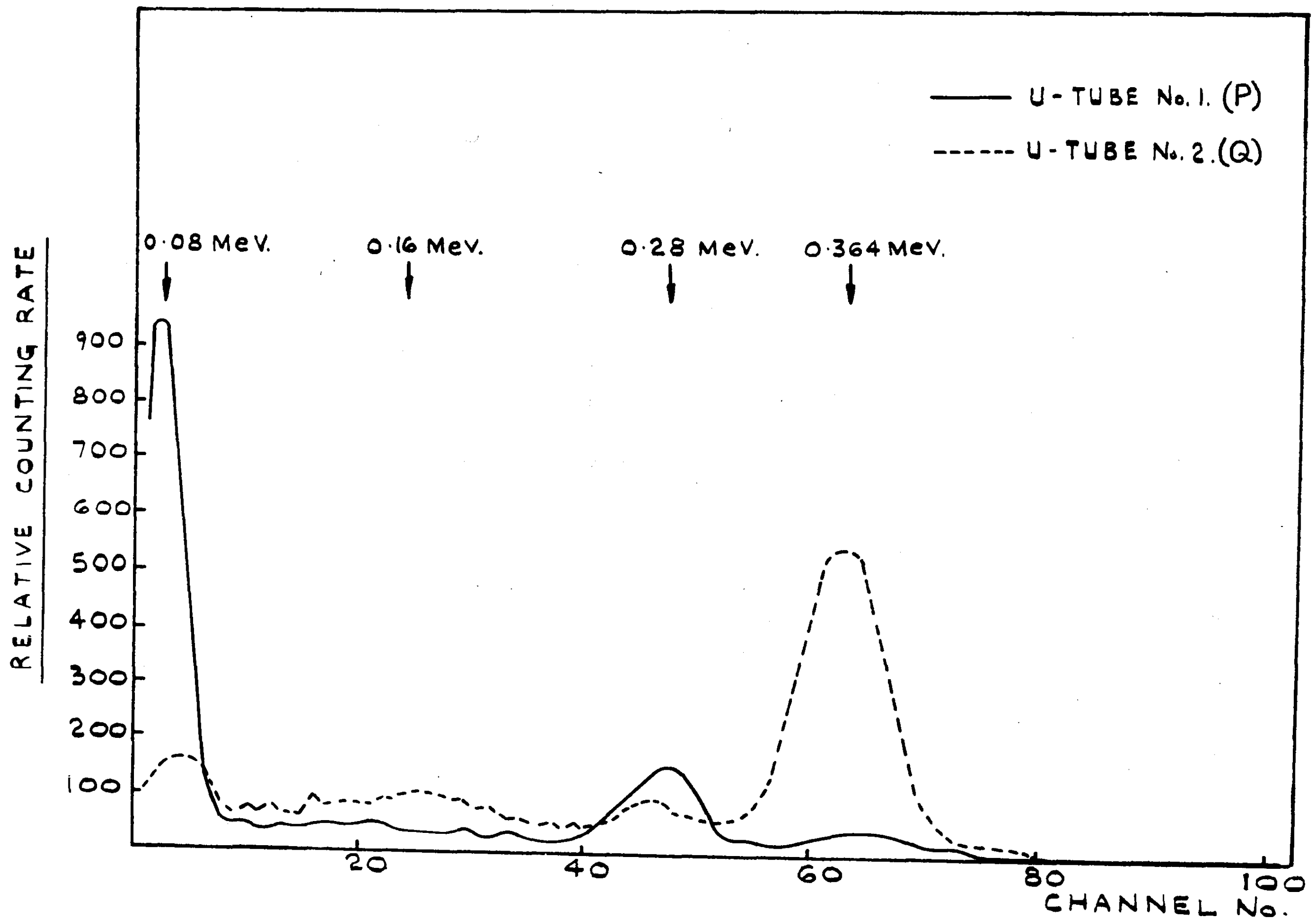

U-TUBE No. 1. (P)
U-TUBE No. 2. (Q)
0·08 MeV.
0·16 MeV.
0·28 MeV.
0·364 MeV.
RELATIVE COUNTING RATE
900
800
700
600
500
400
300
200
100
20
40
60
80
100
CHANNEL No.

FIG. 3,19

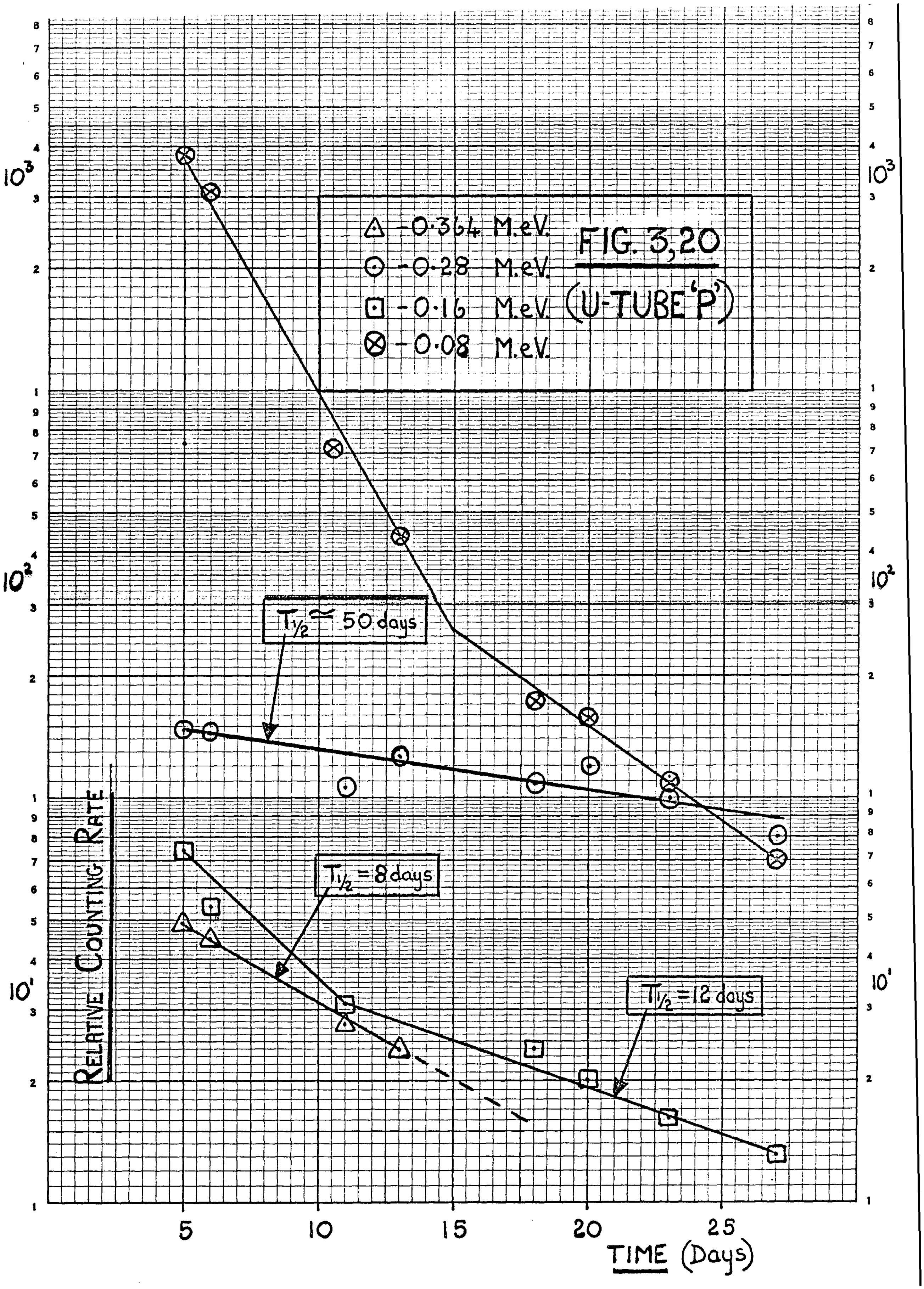


FIG. 3,20

(U-TUBE 'P')

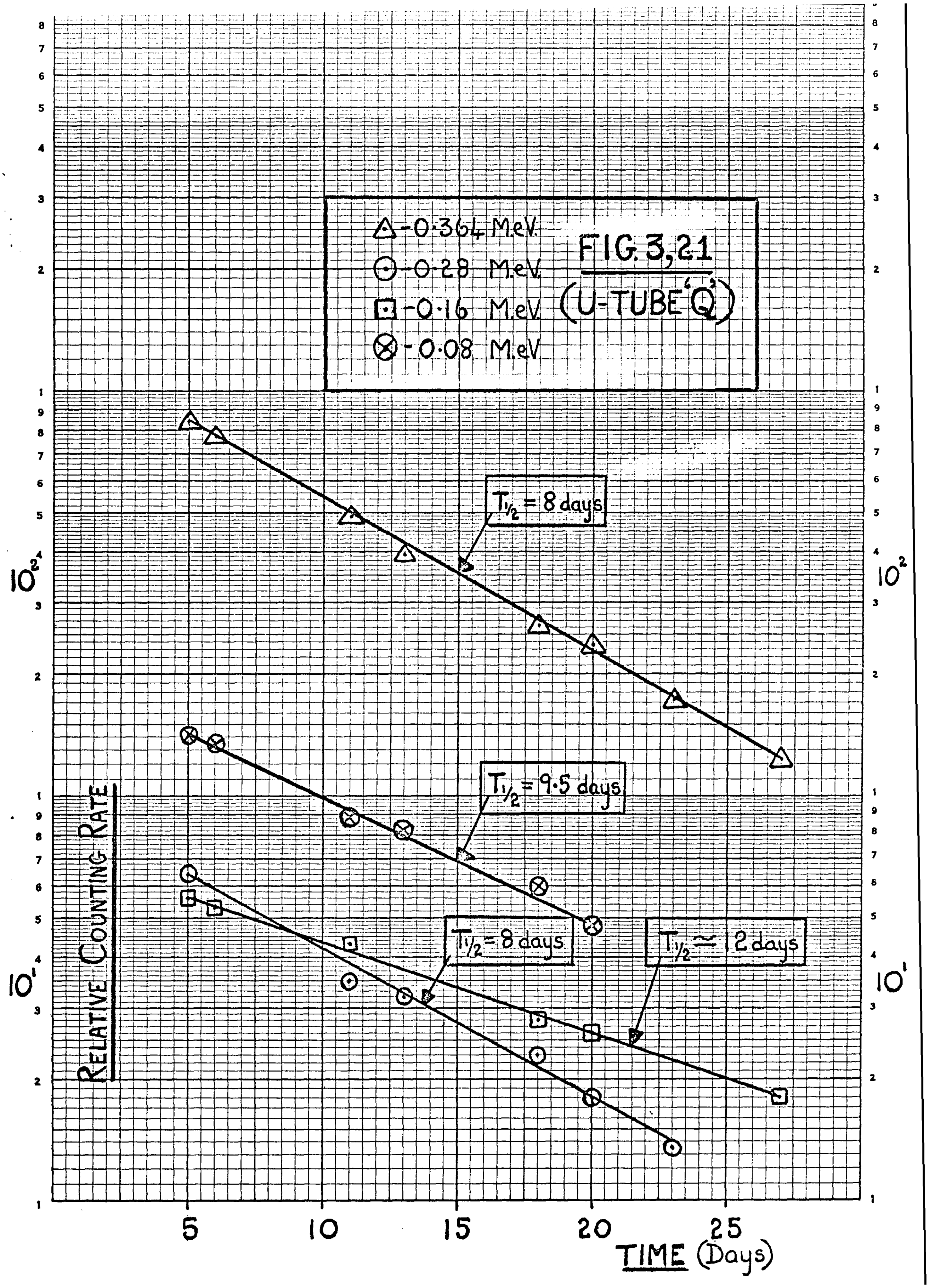


FIG. 3,21
(U-TUBE 'Q')

Fig. 3,20 shows a much more complicated situation; however, charcoal P had insufficient activity to allow these peaks to be precisely characterised. For this reason, we turned our attention to the charcoal sorption pumps A and B, which had an abundance of species producing significant counts, and virtually no I^{131}, as can be seen from Fig. 3,22. This shows the gamma-ray spectrum of Charcoal B, recorded 22 days after the irradiation (Charcoal A was of identical shape). These spectra were therefore recorded at regular intervals over a period of 4 months, and the peaks integrated as described previously. The result is shown in Fig. 3,23 for Charcoal 'A'. (Charcoal 'B' gave almost identical results). From these it was discovered that, after a few weeks, the peak at 0.16 M.eV. became overshadowed by one at 0.12 M.eV., which decayed with the same gradient as those at 0.08 and 0.28 M.eV., indicating that they all belonged to a single parent with a half-life of 50 days. A search of tables of gamma-ray spectra(3,15) failed to reveal any such nuclide.

As a check on the efficiency of the separation technique and on the purity of our iodine-131, a batch of palladium iodide incorporating I^{131} was prepared in the usual way, then dried and left aside in vacuo in the system shown in Fig. 3,18 for 14 days; this was the time calculated to produce a maximum amount of Xe^{131m}.

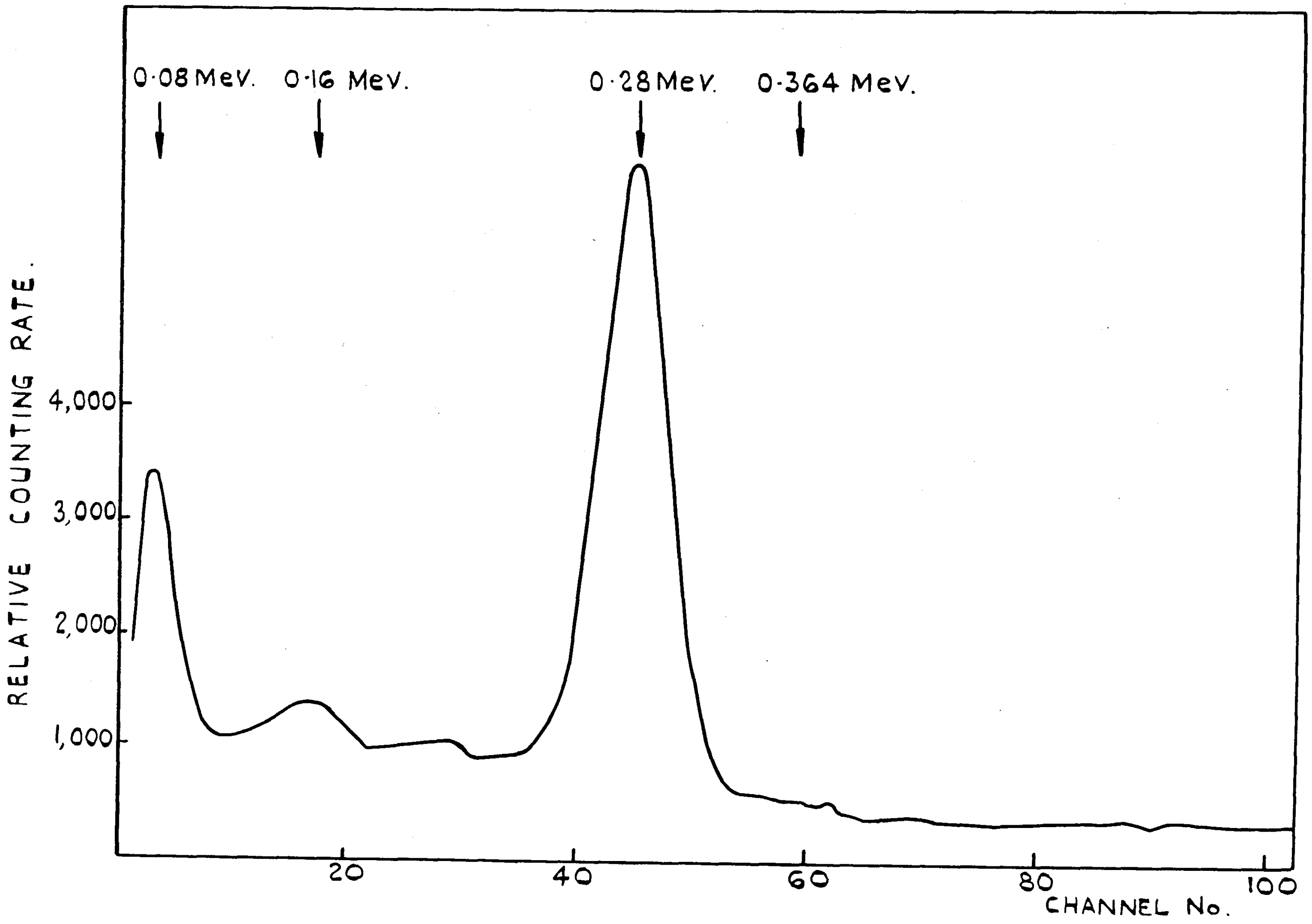

0·08 MeV.
0·16 MeV.
0·28 MeV.
0·364 MeV.
RELATIVE COUNTING RATE.
4,000
3,000
2,000
1,000
20
40
60
80
100
CHANNEL No.

FIG. 3,22

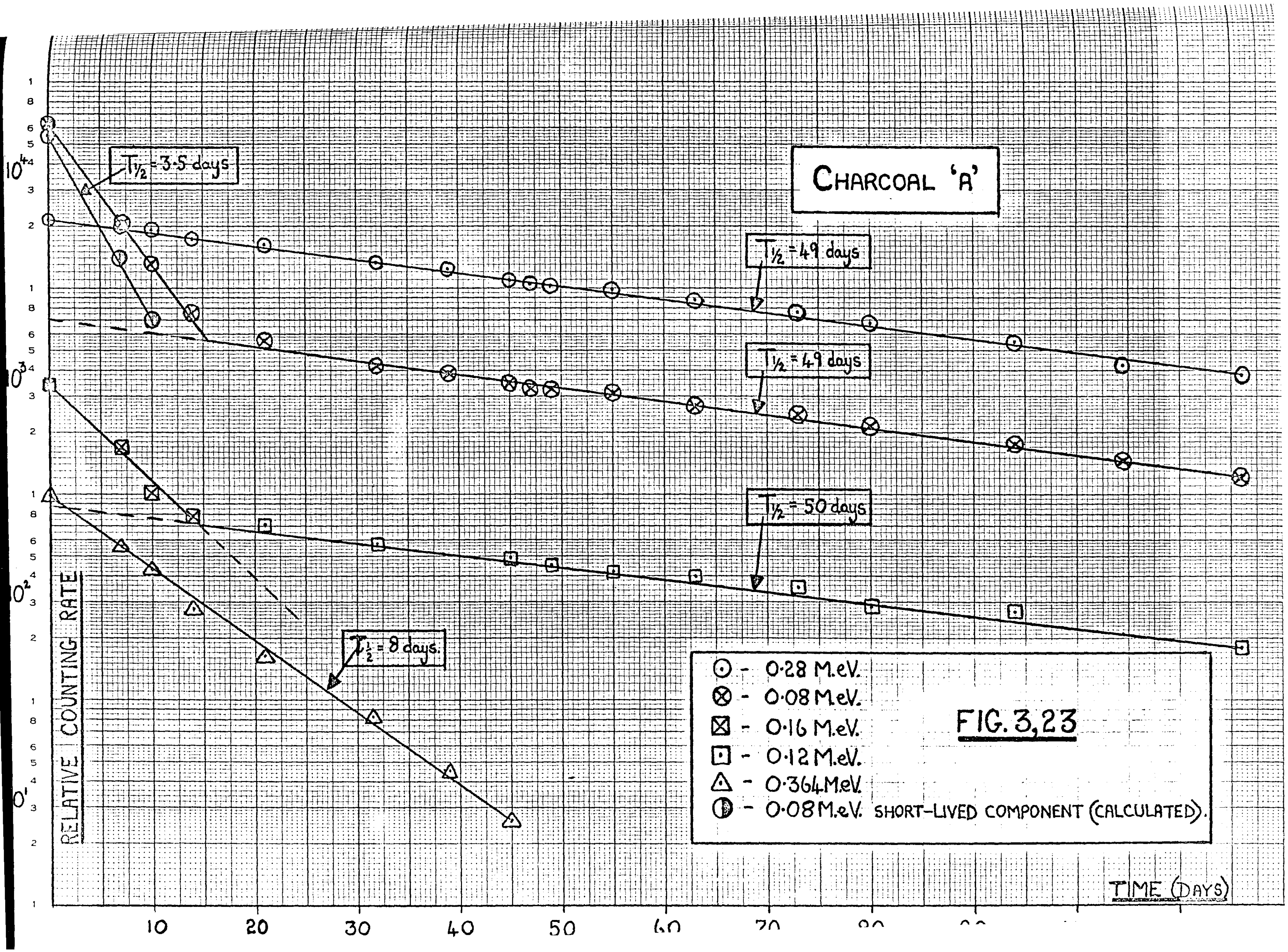

CHARCOAL 'A'
$T_{1/2}$ = 3.5 days
$T_{1/2}$ = 49 days
$T_{1/2}$ = 49 days
$T_{1/2}$ = 50 days
$T_{\frac{1}{2}}$ = 8 days.
⊙ - 0·28 M.eV.
⊗ - 0·08 M.eV.
⊠ - 0·16 M.eV.
⊡ - 0·12 M.eV.
△ - 0·364 M.eV.
◐ - 0·08 M.eV. SHORT-LIVED COMPONENT (CALCULATED).
RELATIVE COUNTING RATE
TIME (DAYS)
10^4
10^3
10^2
10^1
10
20
30
40
50
60
70
80

FIG. 3,23

It was then subjected to exactly the same separation technique as described previously, with the one difference that it was heated to 350°C to effect decomposition. On examination of the U-tubes next day in the scintillation counter, it was found that the first U-tube, P (Fig. 3,24) had collected pure I^{131} (proved by subsequent counting over a period of 45 days), whilst the second U-tube, Q, (Fig. 3,25) contained pure Xe^{131m} (proved in the same way).

<u>Note</u>: The fact that U-tube Q collected the pure I^{131} in the previous experiment whilst U-tube P did so in this one agrees with the fact that the amount of a gaseous component adsorbed per unit mass of activated charcoal is a function of the partial pressure of the component.(3,16)

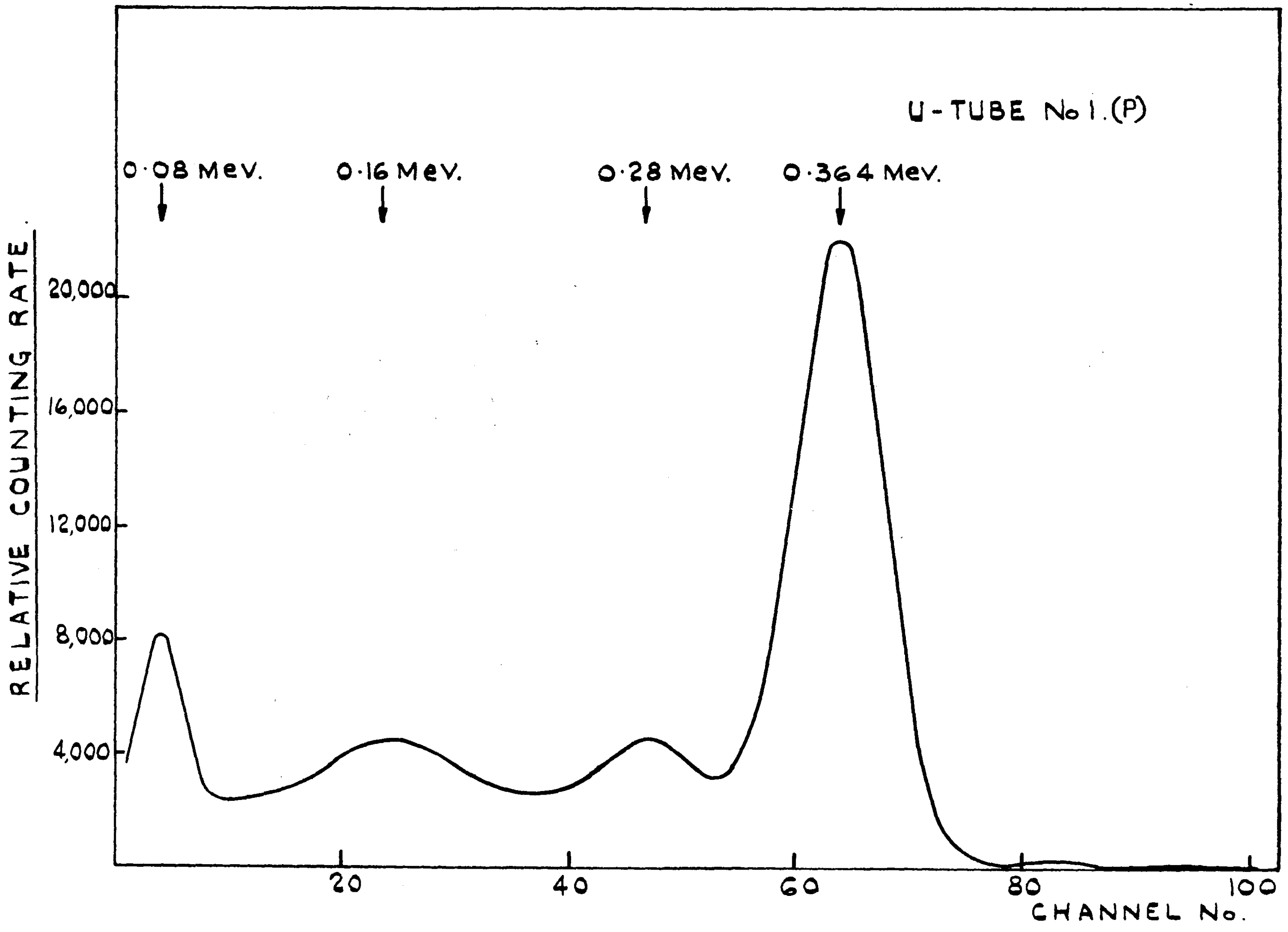
U-TUBE No 1.(P)
0·08 Mev.
0·16 Mev.
0·28 Mev.
0·364 Mev.
RELATIVE COUNTING RATE
20,000
16,000
12,000
8,000
4,000
20
40
60
80
100
CHANNEL No.

FIG. 3,24

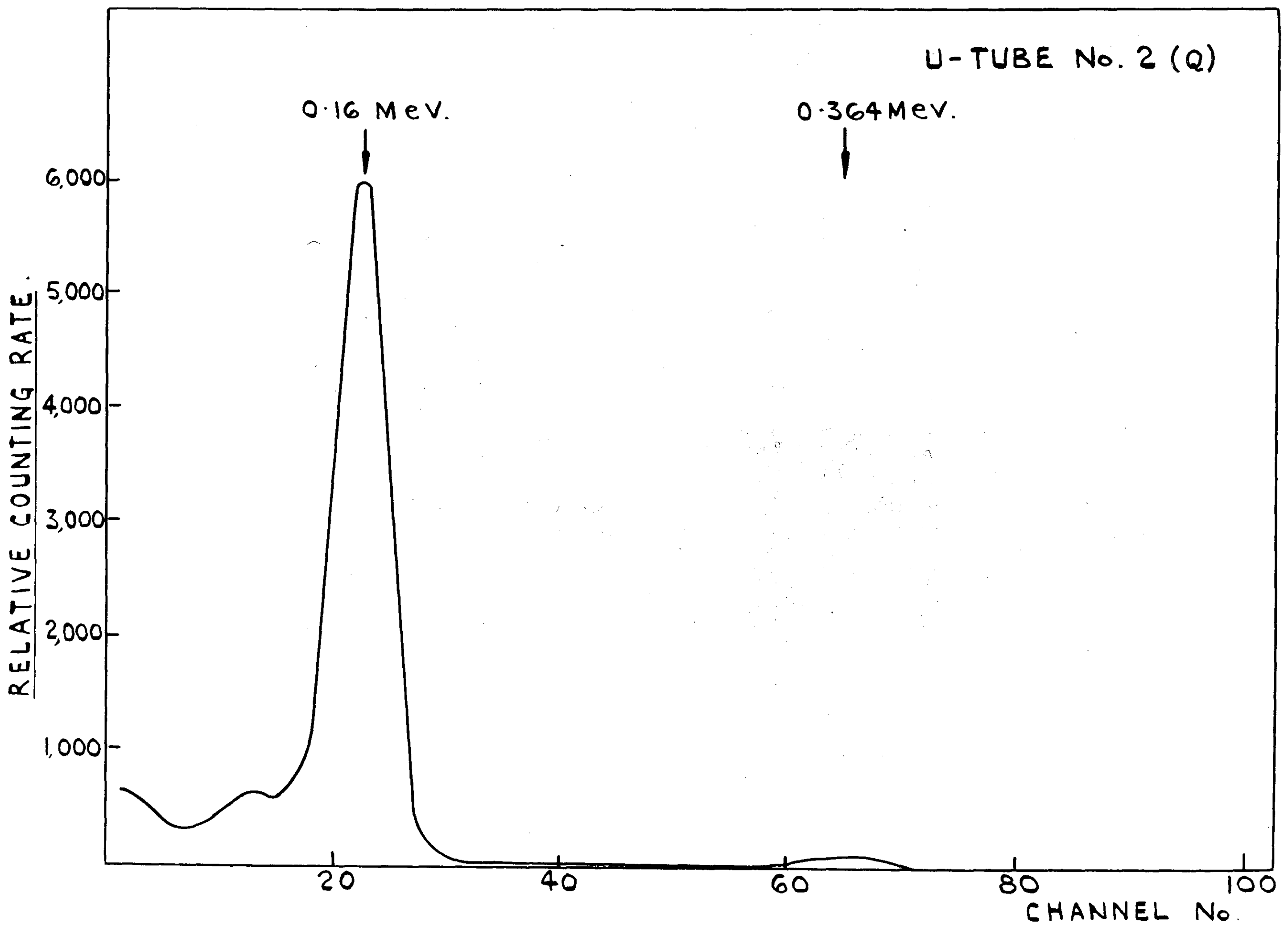

U-TUBE No. 2 (Q)
0·16 MeV.
0·364 MeV.
RELATIVE COUNTING RATE.
6,000
5,000
4,000
3,000
2,000
1,000
20
40
60
80
100
CHANNEL No.

FIG. 3,25

3.22 Modified Unsaturated Polymer Collector Films

As a result of the unsatisfactory results obtained by the use of both metallic and activated charcoal collectors, it was apparent that there was a need for a collector which could chemisorb atomic iodine (charcoal acts by a physical adsorption process) sufficiently strongly to prevent surface mobility of the type exhibited by metallic collectors. Thus the potentialities of unsaturated polymer collectors (Section 3,7) were re-examined.

Because of their inherent lack of elasticity, these films had been bonded to polystyrene by means of chloroform, and had thus been liable to de-gas during neutron irradiation; this was indicated by their subsequent distorted gamma-ray spectra. In spite of this, they had still collected the recoiled iodine in the form of a localised band (plate $3,4^2$). For this reason, it was felt that if the occluded chloroform could be largely eliminated, these collector films could prove to be satisfactory. With this end in view, they were prepared as follows: 7 gm. of butadiene - acrylonitrile co-polymer was dissolved in 150 ml AnalaR chloroform with stirring. Two thin layers of the solution were then painted on to a substrate of pure aluminium (0.002" thick) by means of a camel hair brush, allowing ten minutes between the application of each layer for evaporation of the chloroform solvent.

The mounting of these collector films inside the silica irradiation tube (Fig. 3,9) proved awkward, because the aluminium had insufficient elasticity to expand against its inside walls. This was solved as follows: each collector film was gently fashioned into the form of a loose cylinder, into which was slipped a rubber baloon. They were then both inserted into the tube, and the baloon gradually inflated, thus pressing the collector film against the inside wall. The two edges of the collector film (which had previously been cut to exactly the right size) then came into contact and held the film in position, allowing the baloon to be deflated and removed.

An I^{131}-labelled single crystal of potassium iodide was inserted into each tube, and the charcoal sorption pumps baked out for two days in the usual way, prior to irradiation for 30 minutes in the Thermal Column at a flux of 2.1×10^{11} n./cm^2/sec., using the apparatus shown in Fig. 3,13, but with Drikold round only the charcoal sorption pumps.

On examination of the collector films three days later, it was found that

(a) Their gamma-ray spectra were undistorted, although the peak at 0.08 M.eV. was approximately twice as high as would normally have been expected.

but

(b) Their autoradiographs showed a clear region opposite the crystal (Plate 3,15), indicating that less iodine had been collected there than on the other regions of the film. This was proved by cutting the collector films into three equal horizontal portions, and counting each in turn in the scintillation counter; their I^{131} activities were then estimated by integrating over eleven channels of the 0.364 M.eV. peak. The results for the film whose autoradiograph is shown in Plate, 3,15 were:-

	Relative Activity/Unit Area
Top Region	136.0
Middle Region (Opposite the Crystal)	72.0
Bottom Region	139.5

As a preliminary explanation of this unexpected result, it was postulated that the iodine atoms recoiling from the crystal were too energetic to be caught first time by the collector; they were therefore scattered to other regions of the collector where, having by then less kinetic energy, they could be retained.

It was thus decided to repeat this experiment,

PLATE 3,15

with the following modifications:

(a) A thicker layer of unsaturated polymer on the aluminium substrate.

(b) Drikold completely surrounding the silica tubes during neutron irradiation.

The collector films used in this experiment had the following composition:

	Film 'A'	Film 'B'
No. of Layers of Unsat. Polymer on Aluminium Substrate	5	10

Having employed these in a neutron irradiation under exactly the same conditions as for the previous experiment it was found, on subsequent examination, that in both cases the I^{131} was uniformly scattered over the surfaces of both collector films (as proved by autoradiography and scintillation counting), but

	Film 'A'	Film 'B'
Ratio of $\frac{I^{131} \text{ Collected by Film}}{I^{131} \text{ Collected by Charcoal Sorption Pump}} =$	0.41	1.35

This is in agreement with our postulate that a thick polymer film should be a more efficient atomic iodine collector than a thin one.

The gamma-ray spectra of the collector films were very similar to those shown by the previous ones, the peak at 0.08 M.eV. being again approximately twice as large as would have been expected. However, the charcoal sorption pumps showed more distorted gamma-ray spectra; e.g., in sorption pump 'B', the peak at 0.08 M.eV. was ten times as high as it would have been, had the spectrum been due only to pure I^{131}. This sorption pump was therefore examined in the scintillation counter at intervals over a period of 70 days, when on each occasion its peaks were integrated in the usual way. The manner in which they decay with time is illustrated in Fig. 3,26. This showed that the spectrum was not nearly so undistorted as we had imagined it to be. (Perhaps this was not surprising, in view of the rather large number of layers of unsaturated polymer used, and the consequent risk of occluded chloroform). It proved once more that the peak at 0.364 M.eV. decays with an 8-day half-life which is unaffected by the relative abundances of the other peaks. It also illustrates the initial short-lived region associated with the 0.16 M.eV decay line; this was observed in Fig. 3,20 and undoubtedly accounts for the fact that the 0.16 M.eV. half-life shown in Fig. 3,23 is shorter than it should be.

Thus the experiments described in this section, taken in conjunction with the previous observations on unsaturated polymer collectors (Section 3,7), would lead one to conclude that, in contrast to expectation, the presence of chloroform vapour on the surface of,

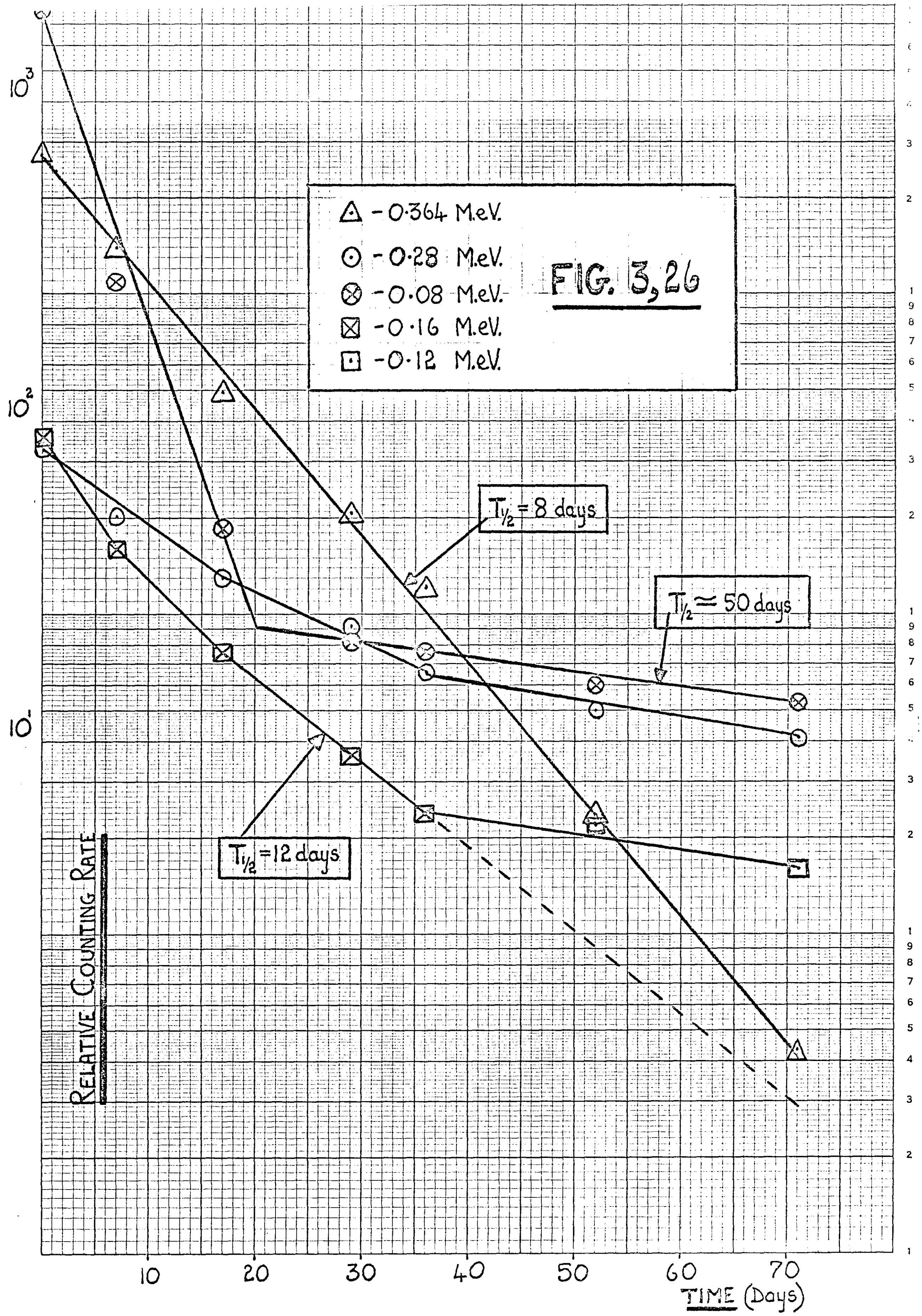


FIG. 3,26

△ - 0·364 M.eV.
⊙ - 0·28 M.eV.
⊗ - 0·08 M.eV.
⊠ - 0·16 M.eV.
⊡ - 0·12 M.eV.
$T_{1/2}$ = 8 days
$T_{1/2} \simeq$ 50 days
$T_{1/2}$ = 12 days
RELATIVE COUNTING RATE
10^3
10^2
10^1
10
20
30
40
50
60
70
TIME (Days)

or in the bulk of the collector film could actually be beneficial; it may have acted as a moderator of energetic iodine atoms, thermalizing enough of them sufficiently to allow their immediate capture on impact; or it may have combined chemically with the iodine via a radiation-induced mechanism. Should this indeed be the case, it would provide us with an explanation for the uniformity of distribution of recoiled iodine on non-degassing collector films. As a test of the validity of this postulate, the following experiment was performed.

3.23. Experiment to Examine the Influence of the Presence of Chloroform

The collector films were constructed as follows: 9 gm of butadiene-acrylonitrile co-polymer was dissolved in chloroform with heating in a round-bottom flask incorporating stirrer and condenser. After dissolution was complete, the hot solution was poured on to an aluminium tray (22 x 14 cm) in a Pyrex dish, covered, and left overnight. By using a hot solution, occlusion of chloroform in the resultant film was encouraged for, as the surface layer cooled, it would deposit a polymer skin, making it more difficult for the chloroform below to escape. Two collector films were cut from this, and the polymer film on each was divided into three equal vertical strips by making two cuts with a razor blade. The two outer strips were then peeled off, leaving the middle one in position, with bare aluminium on either side. On to this aluminium were painted ten layers of unsaturated polymer/chloroform solution, taking care to occlude as little chloroform as possible.

The idea behind this was that if capture of atomic iodine by chloroform really was feasible, then the central region of the film should collect a higher proportion of iodine (perhaps in the form of a band) than those on either side.

These films were then used in a typical irradiation system (Fig. 3,9), surrounded by Drikold. In this case however, the irradiation was conducted in the Central Vertical Stringer for one hour at full power, so as to further encourage de-gassing.

On subsequent examination, it was found that the middle portion of the collector film collected almost four times as much iodine as either adjacent region. However, it did not do so in the form of a band, as may been seen from its autoradiograph (Plate 3,16). This, however, was undoubtedly connected with the fact that its gamma-ray spectrum (Fig. 3,27 , recorded 7 days after the irradiation) was relatively undistorted, as may be appreciated by comparing it to Fig. 3,10.

A repeat of this experiment, with Drikold packed round only the charcoal sorption pumps, yielded very

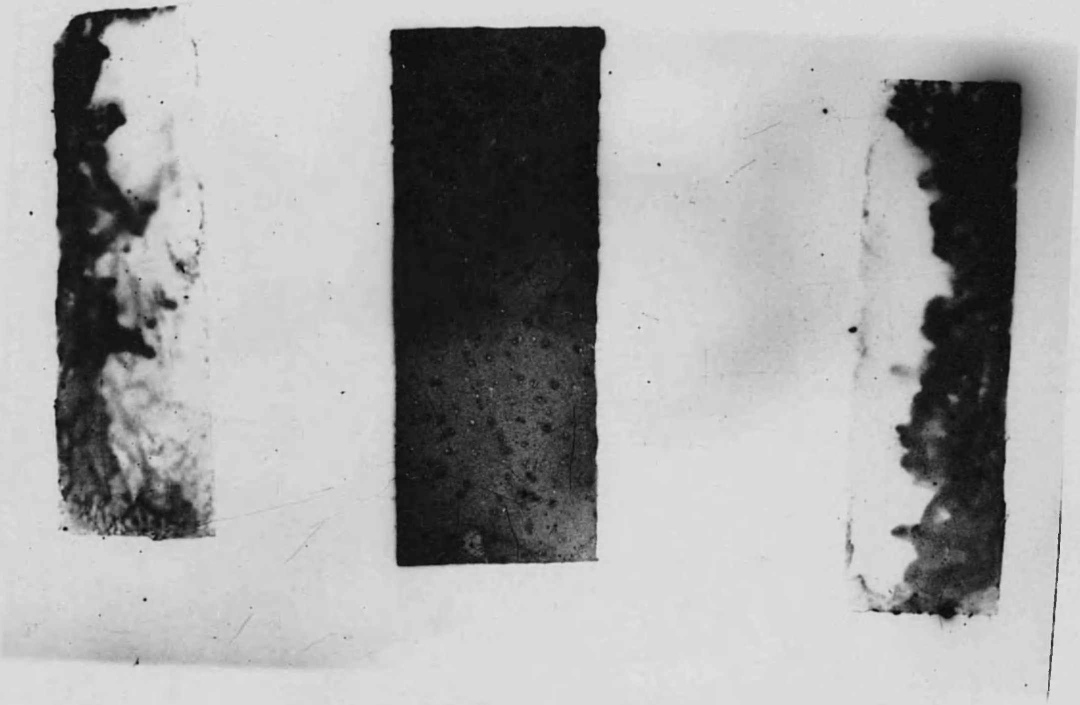


PLATE 3,16

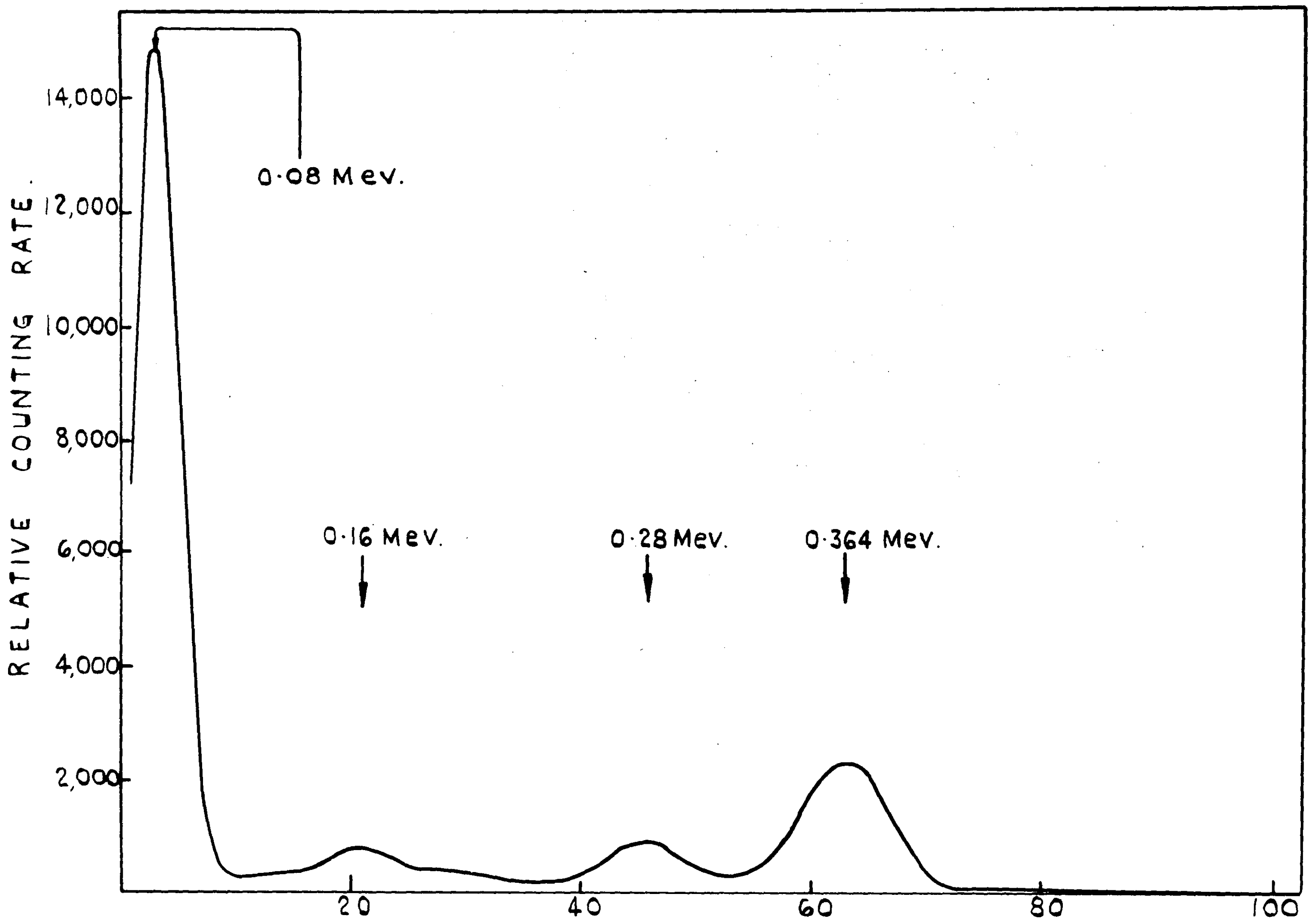

RELATIVE COUNTING RATE
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0·08 Mev.
0·16 Mev.
0·28 Mev.
0·364 Mev.
20
40
60
80
100
CHANNEL No.

FIG. 3,27

similar results.

3.24. The Sorption Ability of Activated Charcoal

It has previously been noted that in systems exhibiting distorted spectra, the enlarged peaks at 0.08, 0.16, and 0.28 M.eV. are present in even greater proportion in the charcoal pumps than on the collector films; indeed, this was the basis for our technique of separation of these extra peaks from pure I^{131}. This fact, together with the constancy of the decay rate of the 0.364 M.eV. peak in the presence of various proportions of the others, shall be employed in the subsequent discussion of the nature of these distorted spectra. In the meantime, the sorption ability of activated charcoal is well illustrated by Fig. 3,28, which shows the gamma-ray spectrum (full line) of an unsaturated polymer/aluminium collector film used as an iodine collector in conjunction with a charcoal sorption pump in the apparatus shown in Fig. 3,9; it is compared with an identical film (dotted line) irradiated at the same time in a Polythene packet. The latter shows a very diffuse spectrum, with only one strong peak at 0.57 M.eV., due to an impurity in the chloroform, which, in the first case, has been adsorbed by the activated charcoal. This is proved by the fact that this activated charcoal showed the same peak, whereas similar batches of activated charcoal used in conjunction with non-degassing collector films displayed no such extra peak.

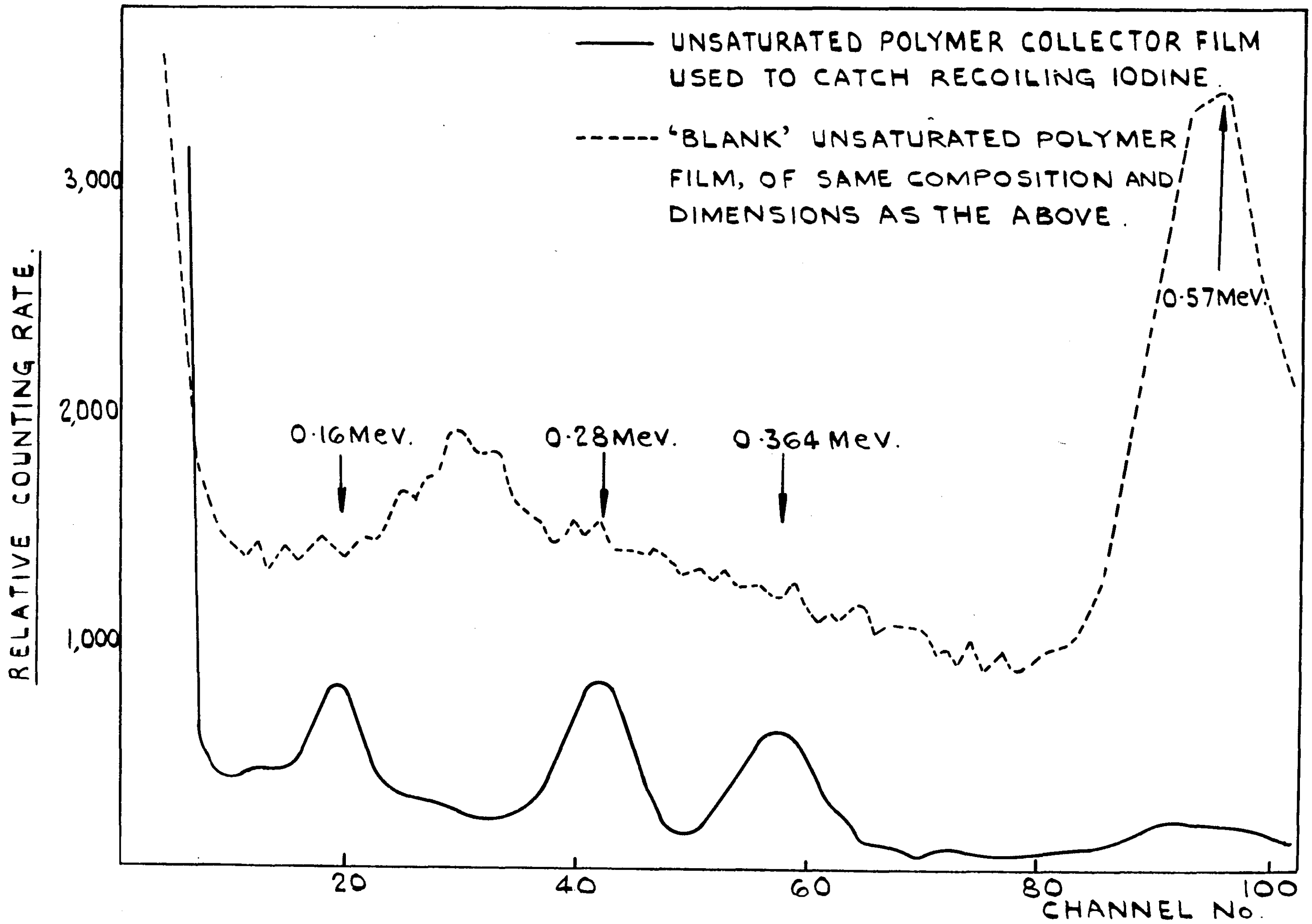

UNSATURATED POLYMER COLLECTOR FILM USED TO CATCH RECOILING IODINE.
'BLANK' UNSATURATED POLYMER FILM, OF SAME COMPOSITION AND DIMENSIONS AS THE ABOVE.
0·16Mev.
0·28Mev.
0·364 Mev.
0·57MeV.
RELATIVE COUNTING RATE.
3,000
2,000
1,000
20
40
60
80
100
CHANNEL No.

FIG. 3,28

3,25. The Production of a Distorted Spectrum in the Absence of any Irradiation (The "Blank" Experiment)

This experiment was performed as a further precaution against the possibility of the high yields, observed by the use of the activated charcoal-Drikold system (Fig. 3,9), being due in some measure to removal of material from the potassium iodide surface under the sorption influence of the charcoal. This would naturally appear to be very unlikely, on the basis of our exchange reaction technique and extensive pre-irradiation bake-out.

Method

(i) Preparation of Collector Films.

7 gm. of butadiene-acrylonitrile co-polymer was dissolved in chloroform with stirring but without heat, over a period of two hours, then poured on to a Pyrex dish and left for two days to allow evaporation of the solvent to proceed. The resultant film was peeled off and stuck on to a piece of pure aluminium foil with the aid of chloroform applied by means of a small brush. Two collector films were cut from this.

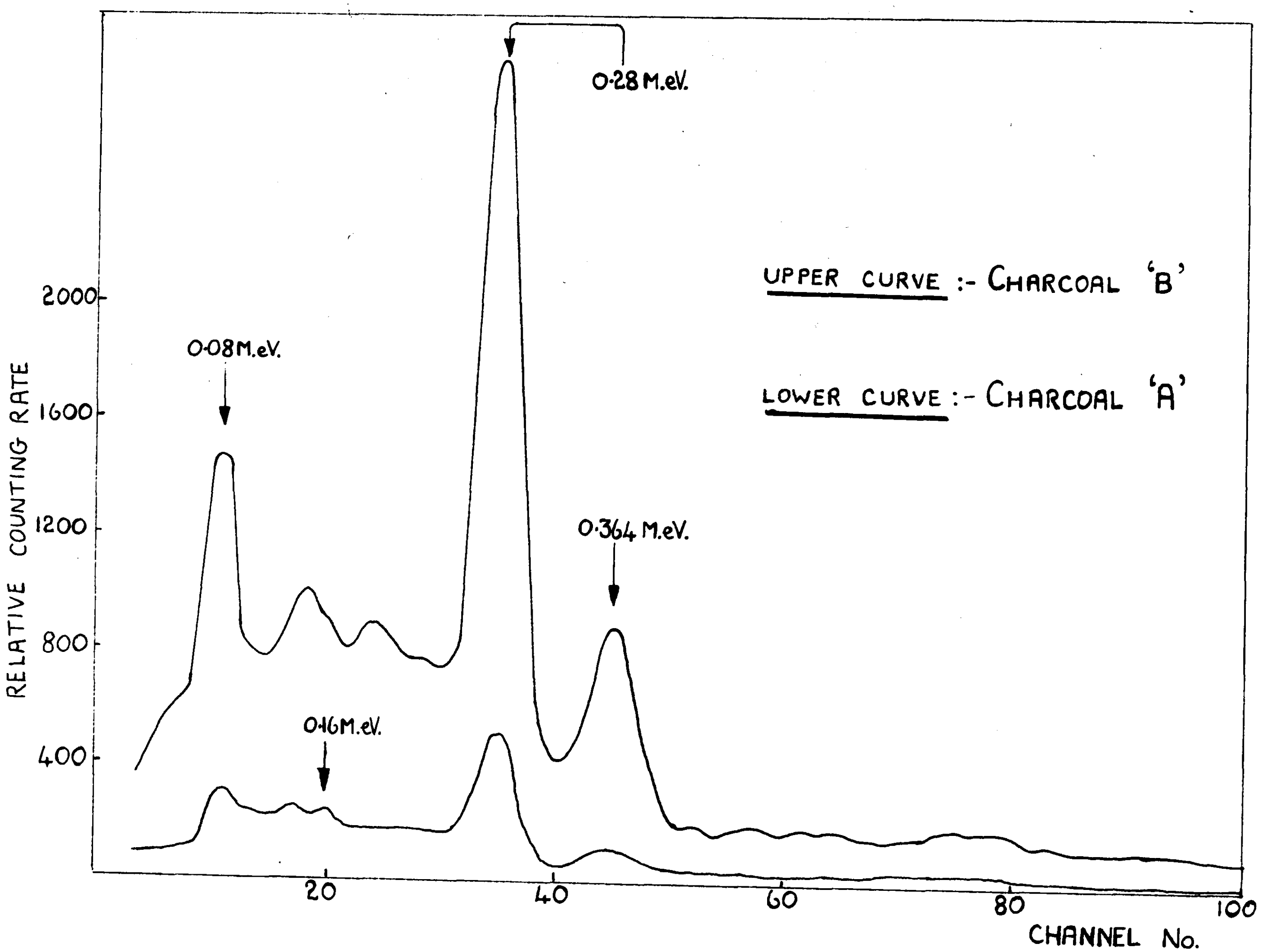
(ii) Preparation of the Crystals.

The single crystals of potassium iodide were polished, sealed in vacuo (10^{-4}Torr.), and annealed at 550°C for 3 days, prior to slow cooling.

These crystals were labelled in the usual way and with their collector films were each incorporated into an irradiation apparatus (Fig. 3,9), which was subjected to the usual pre-irradiation bake-out. They were then sealed off and packed with Drikold into separate Polythene bottles. One of them (A) was merely left aside, whilst the other (B) was irradiated for one hour at full power in the Central Vertical Stringer of the Reactor.

Three days later, each tube was opened. It was found that, as expected, Collector (B) exhibited a distorted spectrum, whereas Collector (A) displayed only about 10% as much I^{131} (as indicated by the 0 364 M.eV. peak area) in the form of an undistorted spectrum. However, to our surprise, the charcoal sorption pump in Tube (A) exhibited a <u>distorted</u> spectrum, although it had not been irradiated. Since the charcoal sorption pump of Tube (B) was still too radioactive to be used as a comparison, both were set aside for a further 22 days, when their gamma-ray spectra were recorded, as shown in Fig. 3,29; from this we see that they both exhibit distorted spectra of almost identical shapes.

Thus, whilst this experiment verified that most of the observed recoils were due to the interaction



0·28 M.eV.
0·08 M.eV.
0·364 M.eV.
0·16 M.eV.
UPPER CURVE :- CHARCOAL 'B'
LOWER CURVE :- CHARCOAL 'A'
RELATIVE COUNTING RATE
2000
1600
1200
800
400
20
40
60
80
100
CHANNEL No.

FIG. 3,29

of neutron irradiation with potassium iodide, it provided an additional valuable insight into the distorted spectra phenomenon. This will be discussed later.

N.B. The gamma-ray spectra of both the crystals used in this experiment were recorded 32 days after the irradiation; this long time interval ensured the removal of all neutron-induced activity in crystal (B). It was found that they both displayed perfectly undistorted I^{131} spectra. This was significant, since we had here a comparison between two crystals, labelled with I^{131} from the same batch of palladium iodide, only one of which was subsequently neutron-irradiated.

This emphasised that the additional peaks in the spectrum could not be accounted for by impurity present in the palladium iodide used to label the crystals.

3.26. An Examination of the Effect of Heating I^{131}-Labelled Palladium Iodide in Vacuo Prior to Labelling Crystals

One of the postulates advanced in an attempt to explain the distorted spectra phenomenon was that it was due to excited states of xenon. However, the extra peaks were present in much greater abundance than could be accounted for by the amount of xenon generated on the crystal by I^{131} decay in the few days between isotopic labelling and their subsequent neutron irradiation. It was therefore concluded that the crystals contained a considerable amount of inactive Xe^{131} which was incorporated during the labelling technique, and subsequently released on irradiation.

As a test of this conclusion, the following experiment was conducted:

I^{131}-labelled palladium iodide was prepared in the usual way, dried by being connected in vacuo through two U-tubes filled with silica gel to a trap of liquid nitrogen, and left overnight. Next day, it was incorporated in the exchange apparatus (Fig. 2,1) and used to label a crystal of potassium iodide (crystal 'A') with I^{131}. This crystal was then removed, and another one (crystal 'B') connected into the exchange apparatus, which was evacuated through taps A and B. Tap B was then closed, and the palladium iodide heated at 200°C for two days at 10^{-4} Torr.: this temperature was too low to cause decomposition, but should have been sufficiently high to remove occluded gases. Crystal 'B' was then labelled in the usual way.

These crystals were incorporated into separate irradiation vessels (Fig. 3,9) with identical palladium-polystyrene collector films, and after the usual pre-irradiation bake-out of the charcoal, were irradiated for one hour in the Central Vertical Stringer. at full power.

Seventeen days later, their charcoal sorption pumps were examined in the scintillation counter (Fig. 3,30). From this it was apparent that Charcoal 'A' displayed a much more distorted spectrum than Charcoal 'B', although they both had collected almost the same amount of I^{131} (as indicated by the 0.364 M.eV. peak height).

This result, taken in conjunction with the observations made in the previous sections, confirmed that the effect was due to a volatile, non-radioactive component (postulated to be Xe^{131}) present in the palladium iodide. This can presumably be incorporated into the crystal during the labelling technique, and on subsequent recoil, with or without irradiation, in the presence of Drikold and chloroform containing films, produce hitherto-unknown excited states.

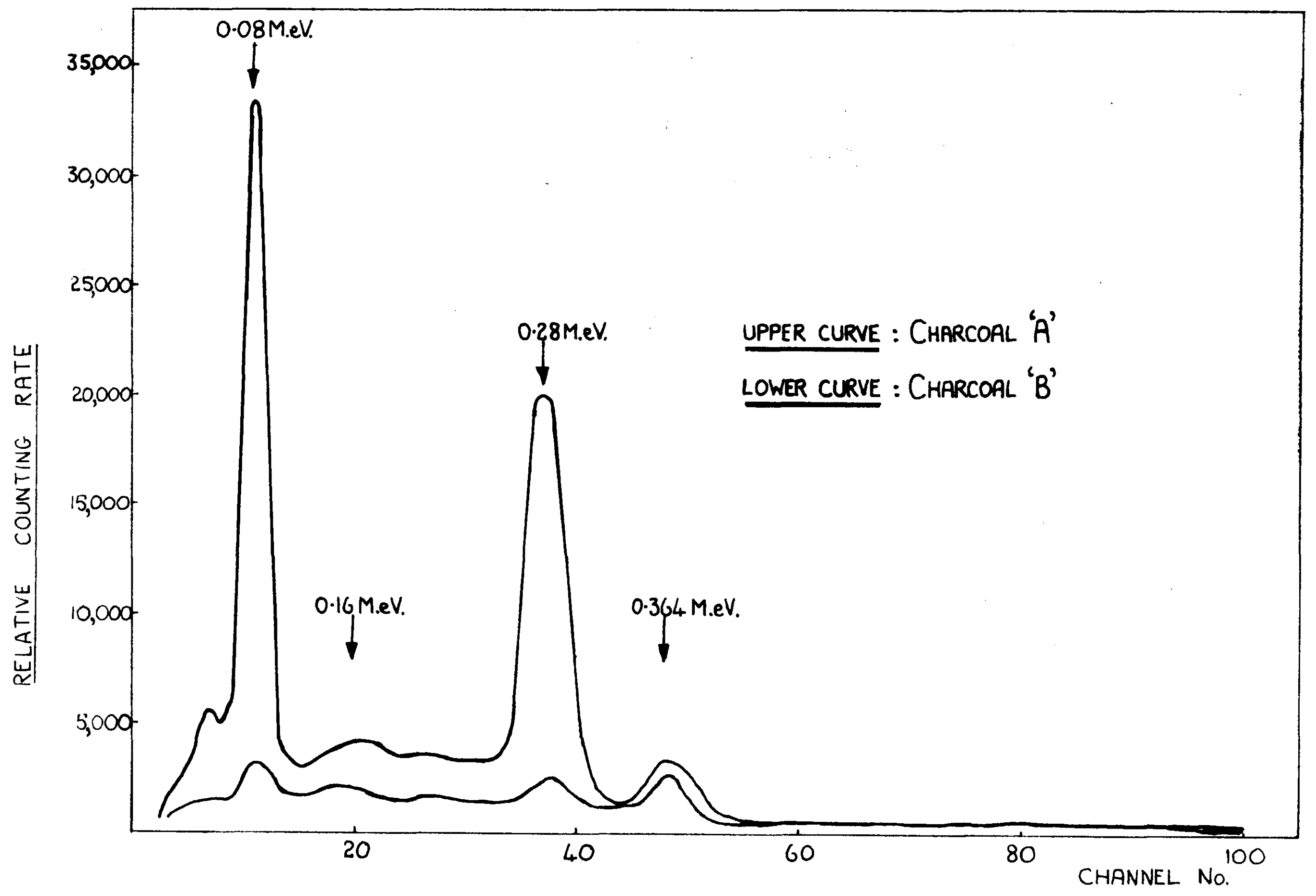

0·08 M.eV.
35,000
30,000
25,000
20,000
15,000
10,000
5,000
RELATIVE COUNTING RATE
0·28 M.eV.
UPPER CURVE : CHARCOAL 'A'
LOWER CURVE : CHARCOAL 'B'
0·16 M.eV.
0·364 M.eV.
20
40
60
80
100
CHANNEL No.

FIG. 3,30

Chapter 4

DISCUSSION

4.1. General Survey

The aim of this study was an attempt to clarify some aspects of hot atom chemistry, as applied to close-packed crystalline solids. We chose to study the effect of neutron irradiation on potassium iodide and predicted that its resistance to radiation damage would be most marked under the influence of thermal neutrons, which would initiate focused collision sequences along the close-packed directions; this would be proved by the ejection of I-131 - labelled iodine surface atoms in preferred directions.

In the course of this investigation we have observed the predominating influence of thermal neutrons, as opposed to fast neutrons or gamma-rays; but the yields of ejected iodine have been surprisingly large. This aspect is of fundamental importance to the interpretation of the effect, and will therefore be discussed at some length.

The contribution made by gamma irradiation to the yields of recoiled iodine has been examined. It will be shown that although this radiation is able to account for only about 10% of the amount of iodine ejected on Reactor thermal neutron irradiation, this is significant; for the mechanisms which explain ejection of iodine on gamma irradiation can be invoked to account for the high yields observed on thermal neutron irradiation, since, in both cases, the starting point is the acquisition of a positive charge by the iodide ion. For this reason, these mechanisms will be reviewed. The contribution made by the results to the field of hot atom mechanistic theory may then be assessed, with particular regard to (n,γ) processes in ionic halides.

A fuller examination of the various ionic conductivity measurements will be made, to clarify the interactions of thermal neutrons, fast neutrons, and gamma-rays on the ordered ionic lattice.

The problem of collecting ejected iodine in the form of a localised deposit under irradiation conditions proved to be very difficult. Thus there were developed a whole series of collector films, only a limited group of which were found to be capable of the desired localisation of ejected iodine; all the members of this group contained occluded chloroform. The influence of the latter in promoting efficient collection of iodine will also be discussed.

In close conjunction with the above observations, it was found that these same de-gassing collectors yielded highly distorted gamma-ray spectra on post-irradiation examination. The separation of the extra components in these spectra has been described; an attempt will be made to elucidate their nature, and their mode of generation.

4.2. A Discussion of the Yields of Iodine Recoiled from Potassium Iodide on Neutron Irradiation, with Particular Regard to the Postulated Focused Collision Sequence Mechanism.

In the Introduction, a case was established for the likelihood of focused collision sequences being generated along the close-packed directions of the iodide lattice in potassium iodide as a result of recoil following thermal neutron absorption. Since then, a considerable amount of evidence has been accumulated which would indicate that this postulate was correct. This may now be conveniently summarised as follows:

(i) In agreement with hypothesis, ejection of iodine from potassium iodide on Reactor neutron irradiation is due mainly to thermal neutrons. (Section 3.12).

(ii) The yields of recoiled iodine are seriously disrupted by the presence of dislocations and substitutional impurities. (Section 3.1).

(iii) On thermal neutron irradiation, high recoil yields are accompanied by low radiation damage, as proved by ionic conductivity measurements (Fig. 3,17), whereas the presence of fast neutrons has been shown to reduce the recoil yields by causing considerable lattice damage.

(iv) The generation of colour centres under certain conditions, and their absence under alternative irradiation conditions has been used to reinforce the above conclusions (Section 3,20).

(v) Chadderton et al(1,24) have proved by computer simulation of radiation damage that focusing is to be expected in this alkali halide.

An estimate of the expected number of iodine recoils due to the generation of focused collision sequences following (n,γ) reaction may now be made :

Dimensions of Crystal = 3.6 x 0.5 x 0.5 c.c.

Total Number of (n,γ) Events to which Crystal is Subjected = 2.61×10^{13}(Equ^{n}4, p.76

Assumed Focusing Range = 10Å

No. of (n,γ) Events Taking Place within 10Å of Crystal Surface

$$= \frac{2.61 \times 10^{13} \times 0.5 \times 0.5 \times 10^{-7} + 4 \times 0.5 \times 3.6 \times 10^{-7}}{3.6 \times 0.5 \times 0.5}$$

$$= 2.17 \times 10^{7}$$

Assuming one ejection for every two (n, γ) events within the Focusing Range,

Approximate No. of Ejections (Predicted) $= \dfrac{2.17 \times 10^{7}}{2}$

$$= \underline{1.1 \times 10^{7}}$$

But Observed Total Number of Iodine
Atoms Ejected = 2.32×10^{17} (Equ^n 5, p.78)

However, this observed value should be corrected for the surface roughness of the crystal. This might be done approximately as follows: the Surface Roughness Factor, which was found to be 7.93×10^2 (Equ^n 8, p.81), is a measure of the extent to which the surface of the crystal departs from the ideally smooth state. This will influence the yield of iodine recoils, for the binding forces which are exerted on a given surface atom by its neighbours depend strongly on its precise surface location; thus the ease with which exposed surface iodine atoms can exchange with iodine molecules is a measure of their subsequent probability of ejection from the surface.

$$\text{Total No. of Iodine Atoms Ejected from Ideally Smooth Crystal} = \frac{2.32 \times 10^{17}}{7.93 \times 10^2} = \underline{\underline{2.93 \times 10^{14}}}$$

Thus, in spite of the considerable volume of evidence for the influence of the ordered crystalline lattice on the yield of recoiled iodine, the observed yields are grossly in excess of those to be expected on the basis of a simple focused collision sequence mechanism. This may be further confirmed by referring to one of the few papers on sputtering yields from alkali halide crystals. In this paper, Navinsek(4,1) reported that on bombarding NaCl, KCl, KBr and LiF single crystals with 2 to 10 k.eV Ar^+ ions, the yield of ejected material was between 0.3 and 2.15 atoms per ion.

At this juncture, however, we may refer to a point already made in the Introduction, viz., following thermal neutron absorption by I^{127}, the resultant compound nucleus will be stabilised by gamma-ray emission, some of which will be internally converted, causing Auger electron emission, and thus the acquisition of a positive charge by the iodine atom. Thus Wexler and Davies,(4,2) in a study of the halogen ejected from gaseous ethyl iodide at low pressures in a vessel fitted with electrically charged collector plates, showed that at least 50% of the I^{128} was positively charged. Thompson and Miller(4,3) proved that the chemical form of a variety of atoms prior to neutron capture had no effect on the charge of the recoil atom; this indicated that the generation of the charge was a nuclear phenomenon. Furthermore, such Auger processes can produce surprisingly high positive charges on the atoms concerned: Snell et al(4,4) have shown that Xe^{131} atoms can, as a result of internal conversion and Auger processes, assume final charges up to +23, the most probable charge being +8. We may thus consider mechanisms to explain how the sudden generation of this positive charge can cause large-scale ejection of iodine; these mechanisms must also take account of the dependence of the yields on the ordered nature of the lattice. In addition, they will be found to account for iodine ejection and colour centre formation by the action of gamma-rays on potassium iodide, since the initial requirement in both cases is the acquisition of a positive charge by the iodine atom. The difference in yields in the two processes will therefore be due to the fact that in the case of gamma-ray interaction, the charges generated will be smaller in magnitude and fewer in number than those produced by thermal neutron absorption followed by internal conversion.

(i) The Varley Mechanism.

This was postulated in an attempt to explain why the number of defects formed by the action of ionizing radiation on the alkali halides is greater than could be accounted for by direct energetic electron transfers. Varley (4,5) proposed that an incident photon would interact with a halide ion and doubly ionize it, (either directly, or by removal of an inner shell electron followed by an Auger cascade), leaving it positively charged. This positive halide ion, located in the field of its six nearest neighbour positive alkali ions, is highly unstable, and so is ejected into an interstitial position; there, because of its strong electron affinity, it traps an electron to become an atom, forming a crowdion (or H - Centre), whilst the resulting halide ion vacancy traps an electron to form an F - Centre.

(ii) Klick's Mechanism.

Using the objection made by Dexter (4,6) to the above mechanism, viz., that the high electron affinity of the positive halide ion would result in its quickly capturing an electron from a neighbouring halide ion, Klick (4,7) showed that the energy released by this electron transfer could be utilised to produce a halogen molecule. This is small enough to fit into the space normally occupied by a halide ion, leaving an adjacent halide ion vacancy. The jump of a neighbouring halide ion into this vacancy results in separation of the vacancy and halogen molecule. Finally, trapping of an electron by each of these defects generates F - and H - Centres.

Figure 4,1(A) illustrates this mechanism:

(a) Ideal crystal before irradiation.

(b) Double ionization of halide ion.

(c) Capture of electron from halide ion neighbour.

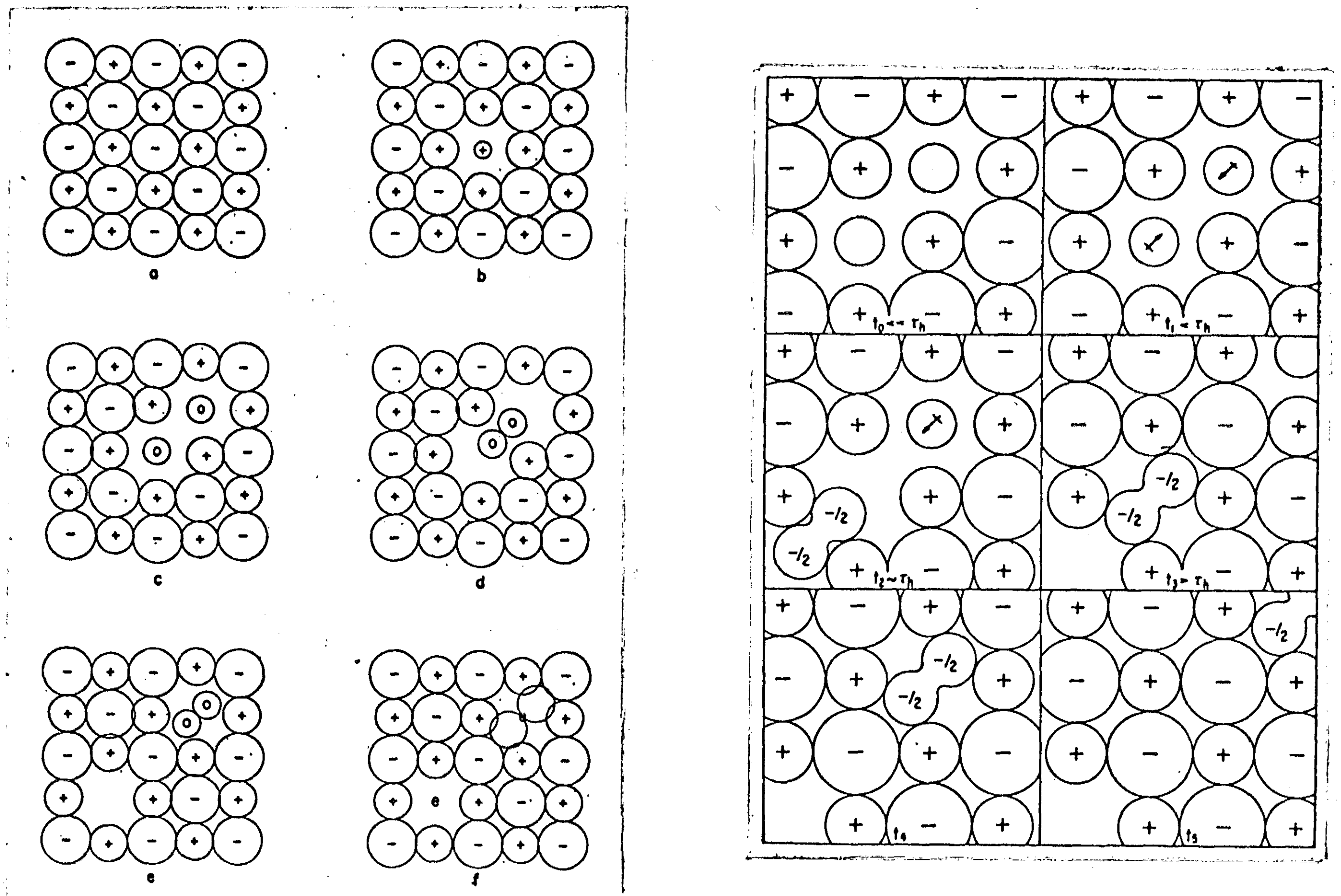
(d) Formation of halogen "molecule".

(e) Jump of halide ion into vacancy.

(f) Capture of electrons to form F - and H - Centres.

(iii) Williams' Mechanism.

Williams (4,8) pointed out that the Klick mechanism would yield F - Centres and H - Centres close to each other, in conflict with deductions made from paramagnetic resonance spectra (Kanzig & Woodruff (4,9)). In his mechanism, shown in Figure 4,1(B), two halogen atoms are formed at adjacent halogen sites (time t_0). Each atom is then attracted to its nearest halide ion neighbour in the <110> direction by an ion-induced dipole force (t_1), which separates the halogen atoms, and imparts kinetic energy to each. The result is the formation of a molecular ion (t_2). The kinetic energy acquired by this molecular ion in the field of the other halogen atom, combined with the energy of formation of the former, is expected to lead to a series of "billiard ball" collisions, thereby separating the molecular ion from the ion vacancy, as shown



(A) FIG. 4,1 (B)

at t_3, t_4, and t_5.

This mechanism is relevant to our studies, because it explains the ejection of halogen from the surface of the irradiated crystal in preferred directions as well as F - Centre formation.

(iv) Pooley's Mechanism.

In a recent paper, Pooley (4,10) pointed out that all of the above mechanisms are of the high energy type, and therefore provide no good reason for the sensitivity of colouring rate to impurities, temperature (4,11), or for colouration by ultra-violet irradiation (4,12). He suggested that F - Centres might be produced predominantly by the radiationless recombination of electrons and holes, followed by a <110> replacement sequence. This mechanism is similar in its net results to the previous one, in that it explains preferred ejection and colour centre formation by the interaction of gamma-rays with potassium iodide, but it would predict higher yields than Williams' postulate. So far as the large number of recoils on thermal neutron irradiation are concerned, the initial step may be described as an "ion explosion", creating a large number of secondaries capable of initiating ejection sequences via, perhaps, by the Pooley mechanism.

4,3. The Implications of These Results in the Field of Hot Atom Mechanistic Theory.

The measurement of retention is still the basic quantitative characterisation of the chemical effect of nuclear transformation. We have chosen to regard retention as being closely related to resistance by the lattice to radiation damage, and have thus been able to estimate its extent by observations of recoil yields, ionic conductivities, etc., without having recourse to dissolution of the target. In this way, we have attempted to relate the hot atom chemistry of potassium iodide to lattice influence effects which are consistent with current ideas on radiation damage. From our studies it has emerged that thermal neutrons can initiate a large number of recoils in potassium iodide without causing large scale lattice damage. However, as explained in the previous section, the yields are too high to be due to simple focused collision sequences arising via prompt gamma-ray emission following thermal neutron capture. Thus it has been postulated that the main reason for the high yields is the sudden generation of a positive charge of considerable magnitude on the iodine atom, due to internal conversion following thermal neutron capture, and it has been shown that the resulting collision chains are consistent with our findings of preferred ejection and modest lattice damage.

This conclusion is in agreement with Walton's assertion (3,13) that many of the observations in hot atom chemistry could be explained more satisfactorily by a process of electronic excitation with consequent rupture of chemical bonds; and he shows that as far as producing electronic excitation is concerned, "recoil atoms are slow lumbering particles of little consequence compared to nuclear transformations". One may therefore recall the rather prophetic statement made as long ago as 1952 by Wexler and Davies(4,2), viz., "If recoil atoms from neutron capture are stopped by collisions before internal conversion occurs, the latter, by producing ions of high charge, will set in train a new series of chemical reactions which must be considered in relation to the billiard ball and free radical processes already under discussion".

Another important aspect of this consideration is that recoil atoms produced via an isomeric transition process are activated chemically as a result of their high nuclear charge, as proved by Iyer and Willard (3,12).

It is thus possible to conclude that the recoil energy and chemical activity of iodine, following thermal neutron capture, is predominantly due to isomeric transition following the (n,γ) process, rather than due to the (n,γ) process itself.

4,4. Interpretation of Ionic Conductivity Measurements.

Potassium iodide crystals irradiated in the presence of Drikold remained colourless and exhibited a lower ionic conductivity in the extrinsic region than unirradiated potassium iodide (Fig. 3,17). This is in agreement with our mechanism, which would produce anion vacancies, with a consequent reduction in the number of cation vacancies, (no. of cation vacancies x no. of anion vacancies = constant.) which in turn control the conductivity in the extrinsic region.

On the other hand, irradiation of potassium iodide in the Central Vertical Stringer of the Reactor in the absence of Drikold, - i.e. in the presence of an enhanced fast neutron flux, produced in the crystals a green colour, which rapidly turned brown when the vacuum in the irradiation tubes was released. This brown colour was due to the presence of free iodine, the production of which would yield a large number of anion vacancies. These are responsible for the increased conductivity shown in the extrinsic range, which therefore displays the same rather high activation energy exhibited by the crystals irradiated in the presence of Drikold. It is believed that as the temperature is raised, the iodine gradually diffuses back into the lattice. This accounts for the gradual return of the conductivity to that of the pure crystal, and for the fact that at the completion of the conductivity run the crystals had become colourless.

A similar line of reasoning can be invoked to explain the comparative conductivity measurements made on un-irradiated and gamma-irradiated potassium iodide (Fig. 3,16). The latter crystals were, prior to the conductivity measurements, faintly brown in colour, and again exhibit this enhanced conductivity - higher activation energy region; at higher temperatures, their conductivity returns to the pure line, and they become colourless. We postulate that these crystals, on being removed from their irradiation tubes, have been oxidised, causing them to lose their F - centres, and liberate free iodine by a reversal of the last two stages shown in Fig. 4,1(A). This would also explain our failure to observe any paramagnetism, and would account for the observation that crystals kept in their irradiation tubes in vacuo can retain their green colour for as long as seven days without any cooling, but rapidly turn brown on being exposed to air.

The interpretation of Fig. 3,5 requires some clarification: from the cation impurity content (P.23), marked enhancement of the conductivity in the low temperature region would not be expected. However, there is an enhancement between 283°C and 417°C which subsequently disappears; this could be due to an increase in the negative ion vacancy content of the lattice, due to the incorporation of a significant amount of divalent anion impurity. This would agree with the reasoning employed in Section 3,1.

4,5. Conditions Necessary for the Localisation of Recoiled Iodine on Collector Films.

One of the main motivating interests in the study of hot atom chemistry is the fact that hot atoms, by virtue of their enhanced kinetic energies and sometimes unusual charge states, can initiate unexpected chemical reactions.

In the system under study, we were faced with the problem of collecting a large number of energetic iodine atoms in the form of a very restricted pattern in an environment of neutrons and gamma-rays; therefore, perhaps not surprisingly, a great deal of difficulty was experienced in restricting these iodine atoms to their initial point of impact on the collector.

The criteria for efficient localised collection of iodine have been deduced from a large number of experiments, among which the following may be emphasised :

(i) Using the simple irradiation apparatus shown in Fig. 2,2, it was proved by shielding experiments (Section 3,8) that not only was the vacuum in the system insufficiently good to prevent gas-phase scattering, but that there was, in addition, a significant amount of surface scattering of iodine over the palladium/polystyrene collectors.

(ii) On using the Activated Charcoal Irradiation Apparatus (Fig. 3,9) in Drikold in conjunction with both palladium/polystyrene and unsaturated polymer/polystyrene collectors, there was obtained (Section 3,9) localised collection of recoiled products (Plates $3,4^1$ and $3,4^2$), and also, for the first time, <u>distorted gamma-ray spectra</u>; the latter phenomenon will be discussed in the following section.

(iii) A series of Thermal Column Irradiations (Section 3.12) yielded the unexpected autoradiograph shown in Plate 3,7. From this, and the irradiation position in the Thermal Column, it was deduced that de-gassing from the collector film was a necessary criterion in the process leading to localised confinement of recoiled species. This deduction was confirmed by the irradiation incorporating a previously de-gassed collector film (Section 3.13) which exhibited much less localisation, and by the use of non-degassing collector films, such as palladium/copper (Section 3.16), Whatman Activated Charcoal Glass Fibre (Section 3.17) and Activated Charcoal/Aluminium (Section 3.18): all the members of this group displayed uniform distribution of recoiled iodine on their surfaces.

(iv) A series of experiments using unsaturated polymer/aluminium collectors underlined the importance of occluded chloroform in the collectors, since, in its absence (Section 3.22), a relatively iodine-free area opposite the crystal was observed.

From these facts it may be concluded that localised collection of "hot" iodine requires the presence of an agent like chloroform to act as a moderator of the energetic atoms, and then (since under Reactor conditions it will probably be fragmented) as a scavenger of the thermalised recoil products.

It is important to note that, should this conclusion be correct, it would indicate the unlikelihood of observing the postulated recoil pattern (Fig. 2,3) on these collectors - a band of iodine opposite the crystal is therefore probably the best one may hope for at the present stage of development of this aspect of the work.

4.6 The Distorted Gamma-Ray Spectra

On neutron irradiation of I^{131}-labelled single crystals of potassium iodide in the simple apparatus shown in Fig. 2,2 in conjunction with collector films composed of palladium/polystyrene or unsaturated polymer/polystyrene, perfect, impurity-free I^{131} gamma-ray spectra had been obtained (Fig. 3,8). However, when identical collector films were employed in the improved irradiation system shown in Fig. 3,9, they yielded I^{131} gamma-ray spectra with grossly enhanced peaks at 0.08, 0.16 and 0.28 M.eV., as shown in Fig. 3,10. Experiments described in Chapter 3 established the following points:

(i) These extra peaks were not due to an impurity in the crystal which was being selectively removed by the collectors, since:

(a) I^{131}-labelled crystals used in experiments yielding distorted spectra were themselves found to exhibit perfectly undistorted spectra,

and

(b) neutron irradiation of unlabelled single crystals of potassium iodide produced only a modest amount of induced activity, which completely decayed within a few days.

(ii) The effect was not caused by any impurity in the collector films since:

(a) the enhanced peaks were strongly localised in the band of recoiled material (see the results on p.51)

and

(b) neutron irradiation of similar collector films produced only short-lived induced reactivity.

(iii) The peaks were not due to an impurity in the activated charcoal sorption pumps, since neutron irradiation of similar charges of activated charcoal induced hardly any gamma-activity.

The first clue towards an understanding of the effect came as a result of the Thermal Column Irradiation described in Section 3.12; it was noticed that the gamma-ray spectrum of the collector film exhibiting the displaced band of iodine was more distorted than the one which collected the iodine in a more localised position (Fig. 3,14). In Section 4.5, it was proved that displacement of iodine towards the top of the film in the former case was due to preferential de-gassing from this region of the film; thus it was postulated that there was a connection between the observation of distorted spectra and the tendency of films to de-gas, which was in turn related to their ability to localise iodine. Thus, it was not unexpected to observe that the gamma-ray spectrum of the palladium/polystyrene film which had been previously de-gassed by heating in vacuo was very much less distorted (Fig. 3,15) and showed little localisation of recoiled species. This interconnection would appear to have been confirmed by the considerable volume of experimental observation incorporating non-degassing collector films, such as palladium/copper, Whatman Activated Charcoal Glass Fibre, and activated charcoal/aluminium, all of which yielded perfectly undistorted I^{131} gamma-ray spectra.

Any possibility of the distortion being caused by neutron activation was finally dispelled by two additional observations:

(i) Gamma irradiation of the system (Fig. 3,9) in Drikold at the Ethicon plant resulted in the charcoal sorption pump exhibiting a distorted spectrum.

(ii) A "blank" experiment in which the system, after prior bake out, was sealed off and merely stored in Drikold for three days without irradiation (Section 3.25 produced an enhanced peak at 0.28 M.eV. in the charcoal sorption pump.

It had been recognised for some considerable time that the extra peaks were not due to iodine, for the following reasons:

(i) The charcoal sorption pumps (Fig. 3,9) invariably exhibited a higher proportion of the extra peaks than the collector films.

(ii) Collector films exhibiting distorted spectra were found, on heating in vacuo, to preferentially "lose" their gamma-ray peaks at 0.08, 0.16 and 0.28 M.eV

Thus, having at this stage eliminated all the obvious explanations based on impurity, and taking into account the fact that the extra peaks displayed exactly the same gamma-ray energy as three of the transitions in the I^{131} decay scheme (Fig. 3,2), it was tentatively postulated that they were excited states of Xenon 131, and should therefore be capable of being separated from I^{131}. This was in fact achieved by use of the apparatus shown in Fig. 3,18, as described in Section 3.21: their half-lives were characterised from the data shown in Fig. 3,23. As a result, we were able to observe three gamma-ray transitions at 0.08, 0.12 and 0.28, all with half-lives of approximately 50 days. Their uniformity of half-life suggested that they all belonged to a single substance; no such substance could be found by reference to tables of gamma-ray spectra.

We may now consider some possible explanations for the effect: thus, let us suppose that these long-lived peaks are in fact part of the I^{131} decay scheme, and are observed only under certain collecting conditions. This postulate suffers from the following disadvantages:

(i) The I^{131} decay scheme is one of the best established ones; thus, if these peaks have been missed by other observers, due to their not having been counted for long enough, etc., then they must be present in very small proportions. This is at variance with our findings, as may be seen from Fig. 3,10.

(ii) On subjecting pure I^{131} to the adsorption technique (Fig. 3,18), we succeeded in separating a single xenon peak at 0.16 M.eV. (Fig. 3,25); this is in agreement with the accepted decay scheme.

An alternative possibility which is offered in a tentative fashion, is that the enhanced peaks are due to previously unknown long-lived excited states of xenon-131. One may envisage their generation as occurring on recoil of xenon towards the collector with absorption of gamma photons from I^{131} atoms remaining on the crystal surface; thus cooling of the apparatus will encourage recoilless gamma-ray emission from the crystal (cf. the Mossbauer Effect). The presence of chloroform would then be necessary to collect the xenon, just as it has been proved able to collect hot iodine atoms.

This postulate does explain perhaps the observation of distorted spectra on gamma irradiation and in the "blank" experiment (Section 3.25), since no neutron activation is involved. It may also account for the high yields, although in this case one must assume the existence of a considerable amount of inactive xenon in the crystal surface layers incorporated, presumably, during the exchange process. This latter postulate would appear to be justified by the observations recorded in Section 3.26, where it was shown that heating of the I^{131}-palladium iodide in vacuo before labelling the crystal greatly reduced subsequent distortion of the gamma-ray spectrum.

On the other hand, the cross-section for such a gamma photon absorption process is bound to be very small; this may be appreciated by a check on the effective cross-sections of the various nuclides which exhibit Mossbauer recoil-free gamma-ray absorption. It therefore seems hardly credible that we should have observed such a strong effect in our simple system.

The complete elucidation of this complex phenomenon would therefore require a considerable amount of further investigation. Some of the proposed future approaches are outlined in the following section.

Proposed Future Work

(i) One of the most significant results to emerge from these studies is that, following (n,γ) reaction, the iodine atom has not only much more energy than has been previously assumed, but, in addition, as a result of its acquired positive charge, should have considerable chemical reactivity. It is thus proposed to extend our observations to a wider class of compounds, to find out if these results are true of (n,γ) reactions in general.

(ii) Considerable evidence has been accumulated in favour of the postulated collision sequence mechanism, by which the close-packed lattice can deal with the sudden acquisition of energy. It is hoped to conduct a review of the known hot atom chemistry of various crystalline systems, and to compare their retentions, etc. with their abilities to exhibit such extended sequences.

(iii) The importance of occluded chloroform collectors in promoting localised collection of hot iodine atoms and in subsequently exhibiting distorted spectra has already been demonstrated. It would therefore be interesting to repeat some of these observations, using palladium/polystyrene films prepared from solvents other than chloroform.

(iv) With a view towards elucidation of the distorted spectra phenomenon, the following experiments are proposed:

(a) It is intended to use isotopically labelled xenon in a simulated exchange technique of potassium iodide single crystals, using the apparatus shown in Fig. 2,1. Subsequent examination of these crystals by gamma-ray spectrometry would prove whether or not they are indeed capable of accommodating a significant amount of xenon.

(b) A strictly controlled quantitative approach to the problem, including mass spectrometry of the occluded products in the charcoal sorption pumps, in an effort to prove whether there is sufficient xenon-131 present to account for our proposed mechanism.

APPENDIX

Measurement of Reactor Thermal Neutron Flux by the Use of Gold Foils

In the example quoted here, two gold foils (A) and (B) were placed in separate irradiation vessels (Fig. 3,9), packed into a Polythene bottle with Drikold, and irradiated in the Central Vertical Stringer at a power of 100 watts for 5 minutes. Their gamma-ray spectra were recorded immediately afterwards via a 64 second count in the scintillation counter and Laben pulse height analyser equipment.

Results:

		Foil 'A'	Foil 'B'
Gross Counts. (Integrated over 21 Channels of 0.364 M.eV. Peak)	=	45,543	45,832
Background Correction	=	3,140	2,384
Net Counts/64 secs.	=	42,403	43,448
∴ Net Counts/sec.		663	679

These values may be converted to Disintegrations/Second by being divided by 0.0504: this factor was supplied by the Reactor Centre Staff, and was derived by them from previous neutron flux callibrations.

		Foil 'A'	Foil 'B'
∴ Activity (A)	=	$\frac{663}{0.0504}$	$\frac{679}{0.0504}$
	=	1.32×10^4 d.p.s.	1.35×10^4 d.p.s

The following relevant nuclear data for the gold foils may be noted:

% Abundance of Au^{197} = 100

Thermal Neutron Cross-Section (σ) = 98.8 barns.

Half-Life of Product Nuclide = 2.70 days

Disintegration Constant of Au^{198} (λ) $= \frac{0.693}{t_{\frac{1}{2}}}$

$= \frac{0.693}{2.70 \times 24 \times 3600}$

$= \underline{2.97 \times 10^{-6}\,\text{sec.}^{-1}}$

	Foil 'A'	Foil 'B'
Wt. of Foil =	42.5mg.	41.6mg.
No. of Au^{197} Atoms Present =	$\frac{4.25 \times 10^{-2} \times 6.02 \times 10^{23}}{197.0}$	$\frac{4.16 \times 10^{-2} \times 6.02 \times 10^{23}}{197.0}$
=	$\underline{1.30 \times 10^{20}}$	$\underline{1.27 \times 10^{20}}$
No. of Au^{198} Atoms Produced on Thermal Neutron Activation ($N^{198} = \frac{A}{\lambda}$) =	$\frac{1.32 \times 10^{4}}{2.97 \times 10^{-6}}$	$\frac{1.35 \times 10^{4}}{2.97 \times 10^{-6}}$
=	$\underline{4.44 \times 10^{9}}$	$\underline{4.54 \times 10^{9}}$

But Number of Au^{198} Atoms Produced on Thermal Neutron Activation is Also Given by the Equation

$N^{198} = N.^{197}\sigma.^{197}\phi.t$ where $t = 5 \times 60$ secs.

and ϕ = Thermal Neutron Flux

$\therefore$ Thermal Neutron Flux (Neutrons/cm^2/sec.)

$$= \frac{4.44\times10^{9}}{1.30\times10^{20}\times9.88\times10^{-23}\times5\times60} \qquad \frac{4.54\times10^{9}}{1.27\times10^{20}\times9.88\times10^{-23}\times5\times60}$$

$$= 1.15 \times 10^{9} \qquad 1.21 \times 10^{9}$$

$\therefore$ Thermal Neutron Flux at 100K Watts. (Full Power)

$$= 1.15 \times 10^{12} \qquad 1.21 \times 10^{12}$$

$\therefore$ Average Thermal Neutron Flux

$$= \underline{1.18 \times 10^{12} \text{ neutrons/cm}^2\text{/sec}}.$$

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