"AN ACCOUNT OF SOME PHYSICO-CHEMICAL INVESTIGATIONS ON GAS-SOLID SYSTEMS"

Thesis

submitted for the Degree of B.Sc.

by

R. W. McIlroy

Jesus College,

Oxford.

Pt. I B.A. (Pt. II) Thesis.

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THESIS

PART I.

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SUMMARY 59

Note: All figures are numbered in order of appearance in a section, prefixed by a number indicating the section, e.g. Figure 2.7 is the seventh figure in Section II.

SECTION I. INTRODUCTION.

(i) Summary of the General Problem.

(a) Objective.

The experiments described in this thesis form a small part of a series of investigations concerned with the separation of certain isotopes on a technical scale. It is intended to effect separation by diffusion through a porous membrane. This method was first attempted by Aston in 1921, who partially separated the isotopes of neon. G. Hertz in 1933 obtained a specimen of deuterium in which no hydrogen could be detected by spectral analysis, by a method involving 48 baked clay membranes in series, the heavier fraction from each being returned to the previous stage, and the lighter sent on to the next, i.e. the total effect was one of transfer of light and heavy fractions in opposite directions (Naturwiss. 21, 884, 1933).

In the present case, however, porous clay membrane was ruled out since it has insufficient mechanical strength for plant application, and the pore sizes are much too large, for the maximum efficiency of separation is attained when the mean free path is of the same order as the pore diameter. (The mean free path of hex at 55° and 20 mms. is of the order of 10^{-4} cms.).

Recourse was therefore had to metal membranes

/which

which could be made quite strong enough to be used in a plant. Many methods are being developed for the preparation of metal membranes with very small pores, of effective diameter well below 10^{-4} cms. Unfortunately most metals are heavily attacked by hex vapour and solid reaction products which may include TX_4, TO_2X_2, CuX_2, NiX_2, depending on the membrane material, are deposited in the pores and reduce the porosity, ultimately to zero. The general problem is to find a membrane material and an appropriate treatment for it which will produce a mechanically strong membrane having the required flow characteristics, and which is also stable to hex within certain limits.

(b) Previous investigations and general results.

Up to 1943, most of the work on membranes was done on the porosity changes resulting from hex action, because the method involved is simple, and therefore quick, and because it was more obviously important at that time to establish that a membrane could be produced which would retain its flow characteristics after considerable exposure to hex.

Using mainly copper and nickel membranes, the changes in porosity were measured (at Oxford) in two ways, each having the same principle which was to measure the porosity, with air, before and after a long exposure to hex at a known temperature. (Oxford Report No. 44, Br-345).

/Method A

Method A, as used by Mr. W. M. Jones, involved exposure to the atmosphere between treatment and porosity measurement, which were done on different apparatus, but since the membrane did not have to be specially supported, large numbers of 1/2" discs could be tested at one time, i.e. under identical conditions.

Exposure to the atmosphere was probably accompanied by hydrate formation which prevented a second experiment being done on the same membrane, i.e. a curve could not be obtained relating porosity loss with time, except by using different membrane samples.

Method B, as used by Mr. L. E. J. Roberts, differed in that only one membrane could be examined at a time since it was supported in a special holder which enabled the porosity to be measured in situ with dry air. The experiment could, however, be repeated and a graph obtained showing the relation between porosity loss and time of exposure. It was also possible to measure the effect of various pretreatments on the porosity.

A combination of these two methods, i.e the large scale use, by Method A, of procedures shown to be valid by Method B, proved very useful in determining the effects of various pretreatments on the ultimate stability of membranes, and also in assessing the behaviour of many different kinds of

/membrane

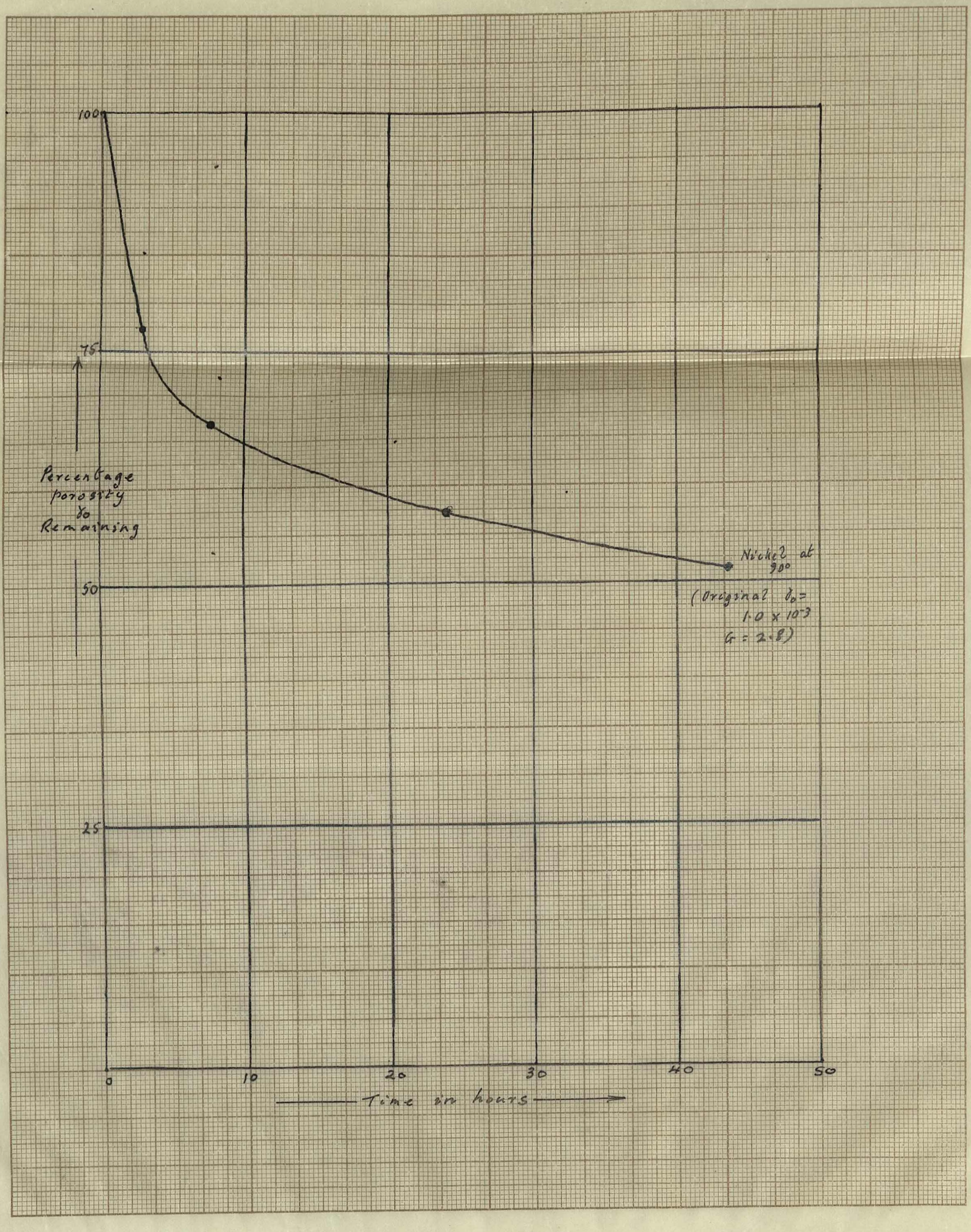

100
75
50
25
0
10
20
30
40
50
Percentage porosity % Remaining
Nickel at 900
(Original δ_0 = 1.0 x 10^{-3} G = 2.8)
Time in hours

FIGURE 1.1

membrane.

In all cases it was found that the relatively large initial drop in porosity was followed by a rapid falling off in rate. For example, the curve for a particular Mond Nickel membrane at 90° is given in figure 1.1.

The rate of attack increases rapidly with temperature, but experiments performed at 3, 18, 50 and 80 mms. indicate that there is no pressure dependence.

For various reasons which do not concern us here, copper as a membrane material was abandoned, and most recent work has been done on nickel. Aluminium, which also shows promise, from the low attack so far observed, has yet to be examined closely.

Plain, untreated nickel, even after extensive degassing is quite useless and various pretreatments have been tried. In America membrane is treated with fluorine, and this appears to cause stabilisation of the same order as oxidation. The method has the disadvantage that wet air must be excluded from the treated membrane.

In Oxford and Billingham, an extremely simple method of stabilisation consisting simply of oxidation in air at 300° or 400° has been investigated. Such a method, besides being simple in itself might have the added advantage of enabling the membrane to be pretreated during manufacture, and then put into the plant without special precautions being taken to keep

it perfectly dry - as are necessary in the case of fluorinated membranes.

Very little is known as yet concerning the mechanism of stabilisation by oxidation, but the following tentative observations have been made (Oxford Report No. 45, Br-428).

1. At 400° the film formed after a few hours is blue.
2. At 300-350° the film formed is yellow. In both cases the compound is probably preponderantly monoxide.
3. The oxidation treatment itself causes a loss in porosity, which increases with the temperature of the oxidation.
4. At 275°, or below, long periods are necessary for sufficient oxidation to occur.
5. No differences in the resistance to hex have been observed between membranes oxidised in laboratory air or dry air, or oxidised in dry air after reduction in hydrogen.

As a result of observations (1) to (4) a standard oxidation technique was decided upon as a starting point, using a temperature of 300° for 3 hours.

It was also found that extensive degassing at 300° before exposure to hex decreased subsequent attack,

/possibly

possibly by the removal of water. It also appeared that exposure to hex for small periods of time (e.g. three exposures of five minutes each) at room temperature followed by thorough degassing, first at room temperature and then with increasing temperature, was beneficial. Whether this simply removed water vapour more quickly than pumping, in which case the same result should be obtained by prolonged pumping, is as yet unknown.

(ii) The Measurement of Gas Consumption as a Method of Investigation.

As soon as it became evident that membranes with good resistance to "plugging" could be produced, attention was turned to the absolute uptake of hex by the membranes. This was of interest from two points of view:

1. Practical.

In the plant all hex which reacts with the walls and membrane represents a dead loss. Engineers calculated approximately that for every milligram of hex taken up per square foot of membrane per day, the plant size must be increased by 10% above the ideal size. This uptake cannot be investigated by the methods so far described, since uptake may continue slowly after a relatively steady value of porosity has been reached. A possible explanation for this has been given as follows (Oxford Report No. 43, Br-317);

/Oxford

Oxford Report No. 44, Br-345, page 4):

1) The initial rapid fall in porosity is due to complete plugging of the smaller pores, at their narrowest points.

2) Then continued attack may occur in the larger pores, without having very much effect on the porosity, and on the remaining surfaces of the pores already blocked and which no longer contribute to the porosity and which cannot therefore effect it.

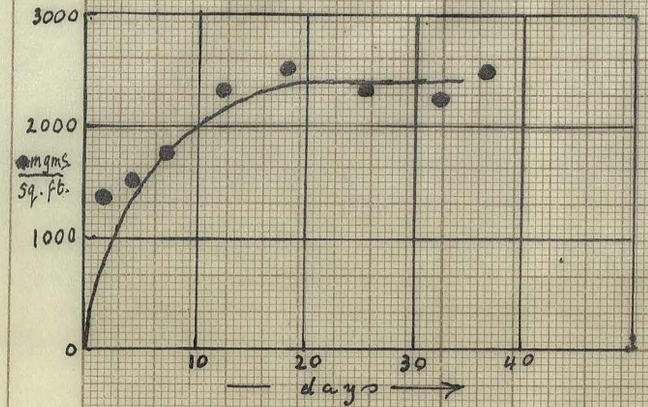
2. Fundamental.

Of less immediate importance is the insight which might be gained into the mechanism of plugging by virtue of the relation between plugging and take-up. One example of the differences which might be expected has just been given.

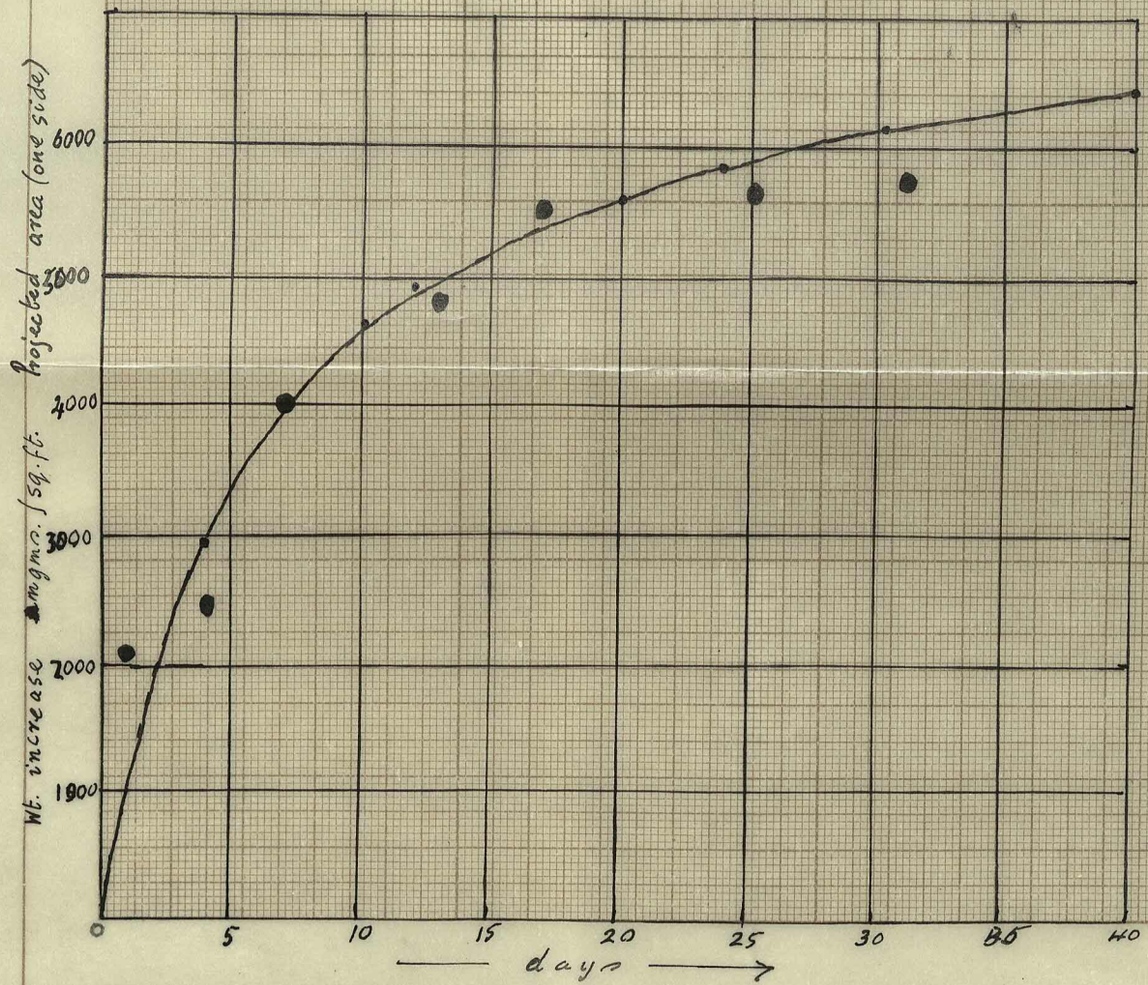
Similarly the effect of hydrogen fluoride, as yet unknown but suspected to consist of catalysis of the hex metal reaction, might be readily investigated by adding known amounts of this gas to pure hex and observing the change in reaction rate.

Also, by observing the uptake during pretreatments with cold hex vapour, some indication might be obtained of how this pretreatment brings about stabilisation. Similar observations on the changes in porosity due to pretreatment suffer from the disadvantage that the changes are rather small and therefore difficult to

/measure



Curve 1



Curve 2

Figure 12

measure with any degree of accuracy.

Attempts have been made at Billingham (Eduljee "The Corrosion of Filters by hex", Br-286, Section III.) to measure uptake by weighing the membrane before and after exposure, loose matter being brushed off before the second weighing. A sample curve is given in figure 1.2, Curve 1, for etched copper.

Recently a more sensitive method has been developed depending upon the extension of a spiral spring of pyrex or silica. This methdd seems to be more sensitive but as yet no attempt has been made to determine the uptake on the spring itself. A curve obtained using a pyrex spring is given in figure 1.2, Curve 2. (Eduljee, Interim Report No. 2, "The Behaviour of Filters in Hex", (Billingham) Section III). This curve is for untreated nickel.

Bradford ("A Comparison of Results with Preoxidised Nickel Filters at Oxford and Billingham", March 4th, 1944, page 2½ has stated (for the uptake on oxidised nickel membrane, using a silica spring) that the initial uptake at 70°, 80 mm. hex is of the order of 500 mgm/ft^2 in the first 2-3 days, followed by a reasonably steady rate of 1.5 - 5 mgm/ft^2/day.

It seemed probable from the early results on weight increase (Eduljee, above) that a method based on the fall of pressure in a reaction vessel containing unsaturated hex vapour, the uptake on the vessel being reduced to a minimum, could be made very much more sensitive than that depending on porosity measurements. Preliminary experiments

/by

by Dr. G. O. Jones (Oxford Report No. 44, Bn345, page 23) confirmed this view.

Further, the method lends itself readily to the measurements (in a few days) of uptake on very stable membranes, which normally take weeks to examine, and the apparatus being simple and entirely of metal, is robust and therefore suitable for very long term investigations.

It should be emphasised that here, as in the porosity measuring methods already mentioned, the tests were performed with static hex as opposed to flow methods which would more nearly coincide with actual plant conditions. This was done in the interests of simplicity and speed which is a very important factor in investigations of this kind.

The problem was therefore to develop the apparatus and experimental method and perform some exploratory work on particular membranes, an account of which forms the subject matter of this thesis.

It happened that at the time the apparatus came into operation the oxidation technique was just being investigated and so, after obtaining uptake curves for untreated nickel for reference, attention was concentrated on oxidised membranes.

(iii) <u>The Plan of the Thesis</u>.

Section II is a detailed account of the development of the reaction vessel, of which the closing valve was the main difficulty, it being already known that the best

/materials

materials (i.e. those having the lowest rate of attack combined with mechanical suitability) were nickel and aluminium.

A complete seal was eventually effected by pressing an aluminium block onto the polished edge of a closed nickel tube (membrane container), and sealing off all small leaks by a rubber washer placed outside the tube. There is every reason to believe that the valve is quite durable and can be used with confidence in tests lasting many days.

A description of the pumping and hex systems is also included together with an account of apparatus maintenance.

Section III is an account of the experimental procedure adopted, with precautions taken against errors, and an estimation of these errors. In particular it should be noted that the effect of hex reaction in the manometer system has been eliminated, and the uptake in the reaction vessel, already reduced to a low value by using ohly aluminium and nickel, has been determined with the same sensitivity as that on the membrane.

It has not been possible, so far, to perform experiments with completely pure hex, but that used was of a constant purity, probably about 98 mol percent.

The results so far obtained are recorded in Section IV and discussed in Section V.

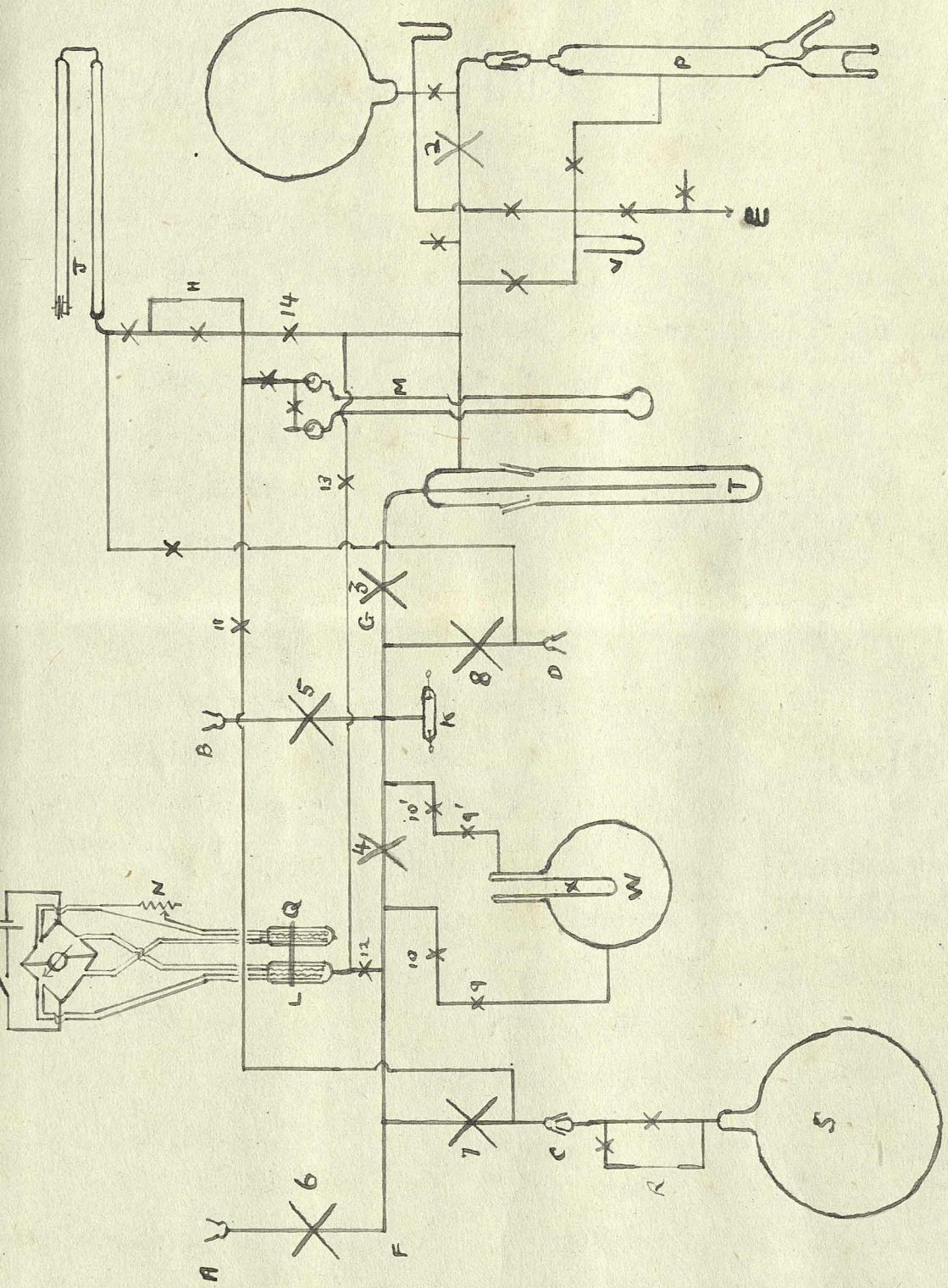


Figure 2·1

SECTION II. APPARATUS.

(i) Pumping System and Preliminary Apparatus.

The pumping system and hex supply shown in figure 2.1 is the unit used in all experiments described hereafter. It consists of a two-stage mercury diffusion pump P, backed by a rotary pump of the "Hyvac" type, connected at E. The low pressure end of the pump is connected through tap 2, to a liquid air trap T, circa 12 inches long and 2 inches diameter, which prevents mercury vapour diffusing into the remainder of the apparatus, and reduces the load on the pump by removing condensible vapours. This is especially necessary in work on hex as mercury and pump oil are attacked. Tap 3 separates the trap from the main line GF, which is divided into two sections by tap 4, on either side of which taps 5, 6, 7 and 8 give access to cones A, B, C and D, for attachment of apparatus to be pumped or supplied with hex. The cone C carries a flask of dry air, S, provided with a capillary R to release air in small quantities. This cone is also connected, by tap 11, to an oil manometer M which can be evacuated via tap 14. Dry air is obtained through the drying train J (calcium chloride followed by phosphorous pentoxide on glasswool) through which the flow is controlled by the capillary H. Final drying may be accomplished by slow passage through the liquid air trap.

/Hex

Hex is stored in the usual re-entrant flask, having two side arms, one in the neck, and one in the body (this being the further from the pump), attached to the main line on either side of tap 4. These arms each carry two taps (9, 9', 10, 10'), arranged so that those furthest from the bottle (10 and 10') are in horizontal limbs to minimise the risk of grease flowing into the tubes during regreasing. The flask is closed by 10 and 10', which means that they need frequent regreasing since hex attacks even Apiezon grease quite considerably. For this operation (only) 9 and 9' are closed. This arrangement enables the bottle to be used for a long period without having to be emptied and exposed to the atmosphere. The bottle contains anhydrous potassium fluoride to absorb any hydrogen fluoride formed, and this formation is reduced to a minimum by "flaming" the bottle and degassing the heated salt before filling with hex. This arrangement of the bottle and cones enables two operations to be very conveniently performed (i) the supply of hex via A in to an apparatus where it is condensed by a "mush" of "Drikold" and alcohol, non-condensible vapours being pumped off via B (4 and 10' closed), and (ii) the return of hex from an apparatus via A, to the bottle where it is condensed by "Drikold" and vapour pumped off via 10'.

The degree of vacuum is estimated by a discharge tube K on the pump side of 4, and a Pirani gauge L

/which

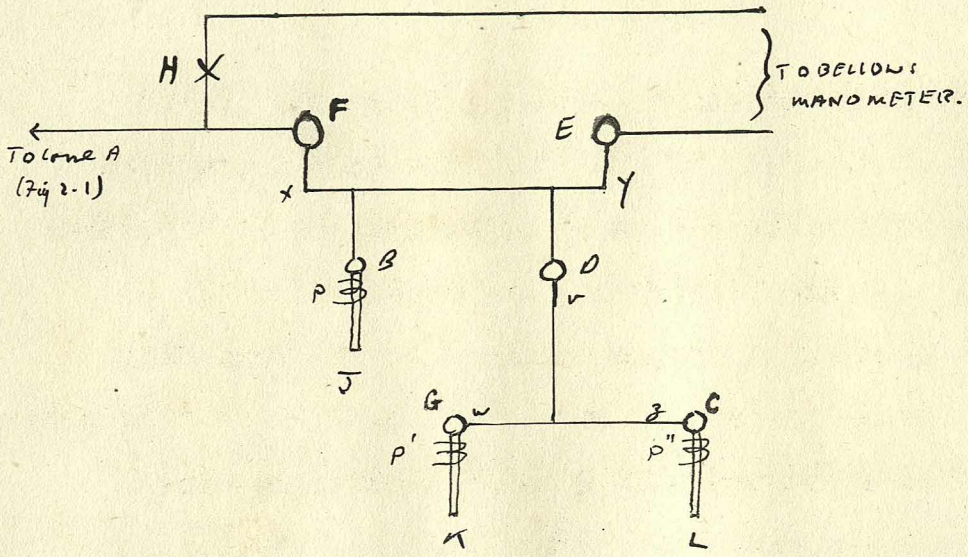


Fig 2·2

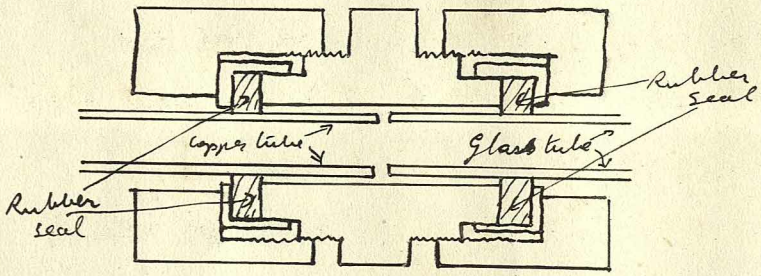


Figure 2·3

which may be connected on either side of the liquid air trap by the taps 12 and 13. The bulb L contains two filaments connected on opposite arms of a Wheatstone bridge. The sensitivity by this method is twice as great as by using a single filament. The remaining arms of the bridge are connected to two similar filaments in a sealed evacuated bulb Q and the gauge is thus temperature compensated. A rheostat N is included in one arm to adjust the zero reading.

Figure 2.2 is a diagram of the apparatus used in the preliminary experiments which were mainly concerned with the construction of a suitable valve for the reaction tube, and although some experiments were done with hex, an account of these will be reserved for the next section. B, D, E and F are ordinary rubber seated isolation valves, soldered to a copper tube XY. F connects to the pumping apparatus via cone A (Figure 2.1) and E connects to the high pressure side of a bellows manometer, the low pressure side of which is evacuated through the tap H. v w z is a glass tube, carrying an isolation valve G and a special valve C, hereafter called "special isolation valve". J and K are closed nickel tubes, circa 12 cms. long and 1 cm. in diameter, which are sliding fits on the outlet tubes of B and G, and sealed to them by black Apiezon W wax. All glass to metal joints are made by black wax, except that at z for which a vac-union (figure 2.3) was used, as C had

/to

to be frequently removed for alterations. The nickel tubes J, K and L all carried spirals of copper tubing, P, P' and P'' as water jackets to prevent damage to black wax or rubber caused by liquid air or furnaces applied to the lower ends of the tubes.

(ii) Elimination of Leaks.

Having set up the apparatus, the first operation is to eliminate all leaks, and the methods used depend upon the size of the leak, and the material in which it occurs. In all cases, however, the leak is first isolated by closing taps successively, gradually working towards the pumps, then,

(1) Very large leaks, e.g. such as prevent the backing pump from levelling the mercury manometer V (figure 2.1) may be found by running the finger over the isolated section until a hissing sound denotes the leak is covered.

(2) Smaller leaks are shown by the mercury pump's failure to lower the Pirani reading. In this case

(a) Glass work is tested for pin holes by the Tesla coil.

(b) Alcohol is poured on to solder and black wax joints, and over tap barrels. The discharge becomes blue when the leak is covered. Or, coal gas or hydrogen may be directed on to the affected parts.

/The

The discharge becomes bluish white when the jet is directed on to the leak.

(3) Small leaks can be detected only when the apparatus has been pumped for a few hours to remove the bulk of the vapours from the walls since these would mask the Pirani reading. By closing taps 3 and 13, and opening 12 (figure 2.1) the Pirani registers the rate of evolution of vapour plus air leak. With 3 open and 2 closed, air leak only is registered, but reliance can only be placed on this, if the difference between the two readings (i.e. vapour) is small. The air leak can also be estimated by closing 2 and 12, and opening 13. In this case, all gas reaching the Pirani passes through the trap, and so should be clean air. Leaks of this type can be found by playing a gas jet over the suspected parts until, when gas enters the leak the Pirani registers a kick due to the higher molecular velocity of hydrogen over that of air. The usual instrument for registering Pirani readings is the milliammeter. If this has a resistance of 80 ohms the full scale deflection represents a potential difference of approximately 80 millivolts across it. By using a milliammeter having a full scale reading of 1-2 millivolts, very small leaks are much easier to find.

(3) Using complicated metal apparatus with many soldered

/joints

joints, extremely small leaks are very difficult to trace and it has sometimes been found necessary to immerse the apparatus in water by degress. When the hole is covered, the rate of leakage suddenly falls, since water has a much higher viscosity than air, and the pressure of air released from the water leaking in is small.

Having eliminated leaks and pumped out for at least one day, until the evolution of vapours is reduced to a very low value on the Pirani gauge, the apparatus is ready for use. Any glasswork to be exposed for long to hex must be "flamed" as far as possible before final pumping, as this eliminates reaction between hex and surface water in the glass, which results in deposition of (probably) TO_2F_2.

(iii) Development of Valves.

Before reliable results could be obtained of the amount of hex taken up by any substance placed in tube L a special isolation valve C had to be obtained which was quite leak proof across, i.e. vapour confined in L must not excape into the apparatus, and there must be no occlusion of gas, e.g. in the plunger, which could not be quickly pumped out. Each of the valves, about to be described, was therefore tested as follows: An atmosphere of dry air was placed in L, C closed and the apparatus evacuated. The rate of leakage of air into the apparatus was measured every hour as for ordinary

/leak

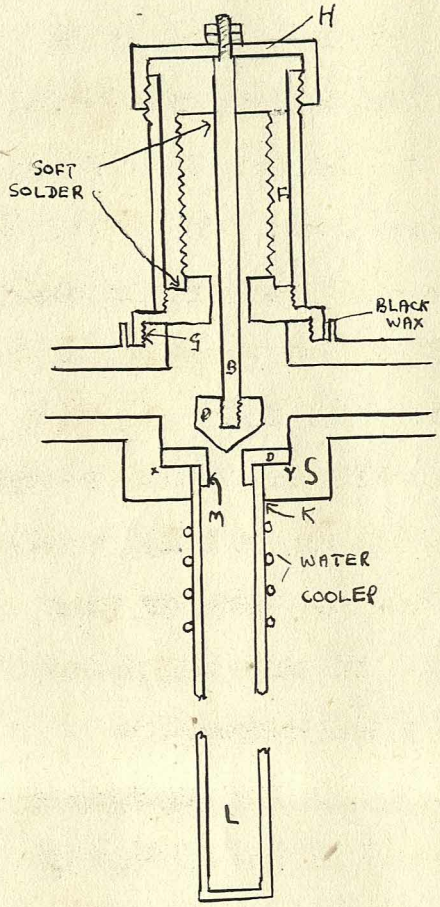


Fig. 2·4

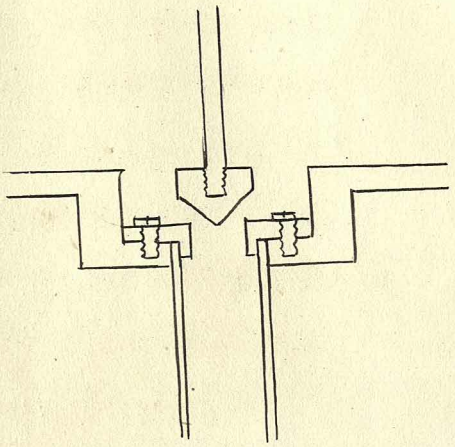


Fig. 2·5

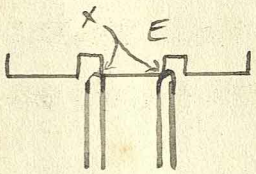


Fig 2·6 a.

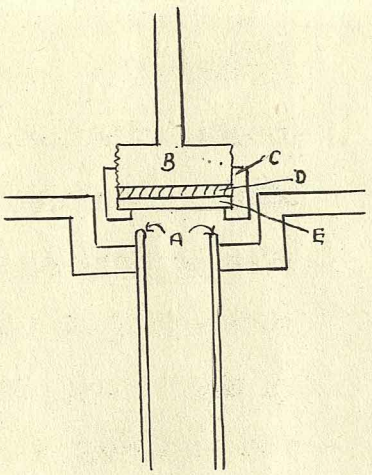


Fig. 2·6

leak finding. The final steady value reached after several hours' pumping showed a leak across the valve. To make quite certain that this was not due to trapped air, the entire system (i.e. valve C open) was evacuated until the Pirani showed no leak, and C was then closed. One atmosphere of dry air was let in for several hours (depending on the suspected size of the leak) and then removed. Pumping was continued until the Pirani showed no rise. C was then opened and the air in L measured, either by the Pirani with F (figure 22) open, or with the bellows manometer (F closed). If this suggested the presence of a leak, the tube L was thoroughly degassed for about 24 hours at 90°, and the experiment repeated. Further repeats with air on for different times, differentiated between a true leak across in which the final reading would be proportional to the time of exposure, for small leaks, and phenomena due to trapped air in which the reading would become constant. In all cases, the apparatus was tested before and after for external leaks.

Besides these experiments, tests were made during hex experiments and will be described in the next section.

The first special isolation valve used on tube L is shown in figure 2.4. It consisted of a nickel tube of 1/32" thickness and 7/16" internal diameter, inserted tightly in the brass valve body S, and hard soldered at K. The surface AY was ground flat and an aluminium washer D

/which

which just fitted the valve body S, and having a flange M fitting the nickel tube, was pushed down to occupy the position shown. The valve was closed by a conical nickel plunger P screwed onto the brass rod B of an ordinary bellows isolation valve. The bellows F was fitted to the valve body by a thread G, sealed by black wax, and the valve was closed by screwing up the cap H by hand.

This valve was used for several weeks in experiments on the calibration of the manometer and hex investigations, and was found to develop a small but distinct leak across, probably due to the aluminium washer being deformed by the plunger, resulting in leakage below it, i.e. between the washer and the top of the nickel tube, not between the plunger and the washer. The washer was therefore firmly held down by three screws as shown in figure 2.5. It was then found necessary to close the valve by wrenches to reduce a large leak across, probably by moulding the washer and plunger together. It was not possible to pump down until the Pirani showed no leak, and on leaving overnight with F (figure 2.2) closed, the bellows manometer showed a pressure of 0.6 mms. Hg. Evacuation of the entire apparatus showed no external leaks. Now in this case, there was no evidence of air being trapped anywhere, i.e. complete evacuation was effected quickly, and therefore the apparent leak could not be explained by assuming air to be trapped beneath the washer. The valve was then

/removed

removed from the apparatus and placed in a press to force the plunger to mould the washer. The leak across was found to be increased slightly.

This valve was of course very similar to the ordinary needle fine control valve, and unquestionably could have been made to work, but three points had to be borne in mind throughout the investigation.

(i) The dosing mechanism had to be simple and therefore excessive pressure could not be used.

(ii) The channel, when the valve was open, had to be large.

(iii) Only aluminium and nickel could be used, and aluminium is very deformable.

It was decided therefore to discard this type of valve altogether, and that shown in figure 2.6 was tested. In this the nickel tube projected above the base of the valve body by 1/8" and the top edge was rounded and highly polished (A). The plunger was the same as in the latest isolation valves in use, a flanged brass ring C holding a rubber washer D on to the bellows shaft B, but below the rubber, and held also by the ring C was a thin washer E of aluminium or lead foil, or ordinary silver paper. In all three cases pressure on the nickel tube punched the washers, and so a disc of aluminium 3/64" thick was used. This was not mechanically damaged except that a shallow groove was cut by the nickel, which was probably of value in

/making

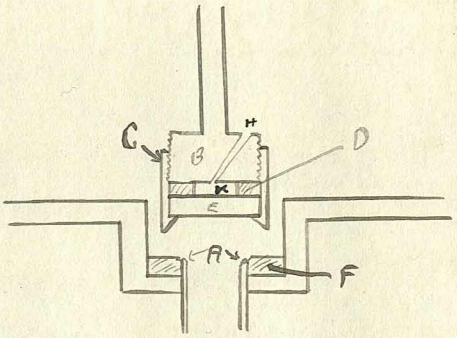


Fig. 2·7

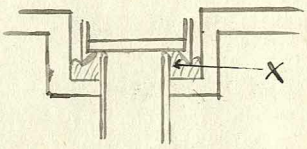


Figure 2·8

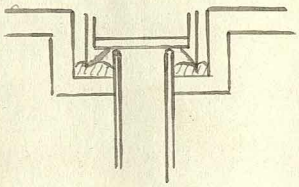


Figure 2·9

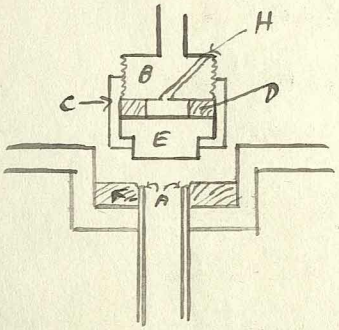


Figure 2·10

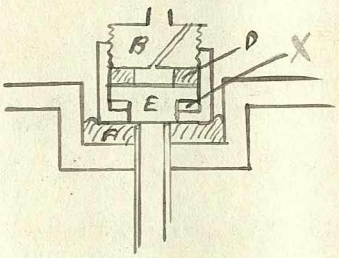


Figure 2·11

making the seal.

However, there was a considerable leak across, probably due to a number of different grooves being cut resulting from sideplay in the plunger. (Several distinct grooves could be seen.) A deliberate groove was therefore cut on the lathe, of such a diameter that contact should occur at an edge (x figure 2.6a). The leak, though smaller, persisted, and it was therefore decided to use this valve, but with a rubber seal to eliminate small leaks, since although rubber could not be used as a washer, the small area in contact through a leak in the nickel - aluminium seal should have an effect less than experimental error.

For this purpose, the ring C was bevelled and the rubber washer F placed round the nickel tube, projecting 1/64" above it, as in figure 2.7. It was hoped that by this arrangement the rubber would be pressed into the space X (figure 2.8), between C and the nickel tube, sealing the joint. The rubber cushion between the bellows shaft and the aluminium was replaced by a rubber ring D and a vent H let in B to pump out the space K, to reduce space in which gas might be trapped.

There was still, however, a small leak across. The least improbable channel being between E and C though it had been hoped that compression of D would prevent that. If this were so, it meant that the space X

/was

was not being filled, i.e that C was simply pressing F downwards as in figure 2.9.

An attempt was made to overcome this by removing the bevel from C and raising the centre of the aluminium washer to project 1/32" below C as in figure 2.10. On screwing down the cap the first pressure would be taken by E on F followed quickly by contact between E and A. This should provide a good seal made absolute by pressure of C on F, which followed further screwing of the cap. Now for this to occur, the ring D would have to be compressed, since E cannot move any further, and a space would occur between C and E as at X in figure 2.11. It is not to be expected that this valve would have a leak between C and E as happens in the valve shown in figure 2.7, because in this case D was highly compressed as it transmitted all the pressure from B to E, whereas in the previous valve it is probable that C and F met before E reached A, so that D was barely compressed at all. In fact the valve was found to make a very good seal, by measuring a leak of air <u>out</u>, but when when the tube was evacuated and the leak <u>in</u> measured, the bellows manometer recorded 3.3 mms. on the scale, after 9 hours' exposure to 1 atmosphere (1 cm. on manometer scale = 0.32 mm. Hg.)

The tube was degassed at 90° overnight and the experiment repeated for 2 and 6 hours. In each case, 3.9 mms. were observed. It was obvious therefore that

/we

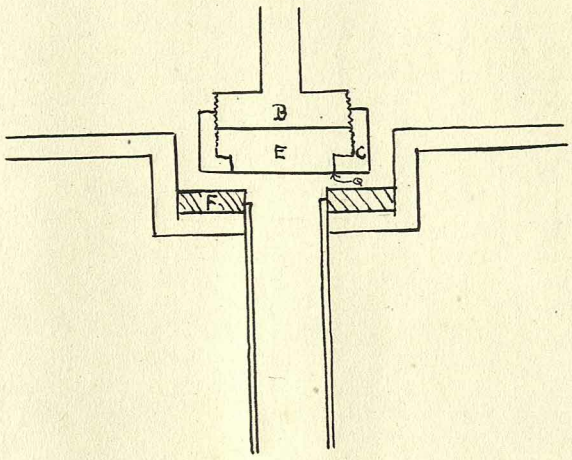


Fig. 2·12

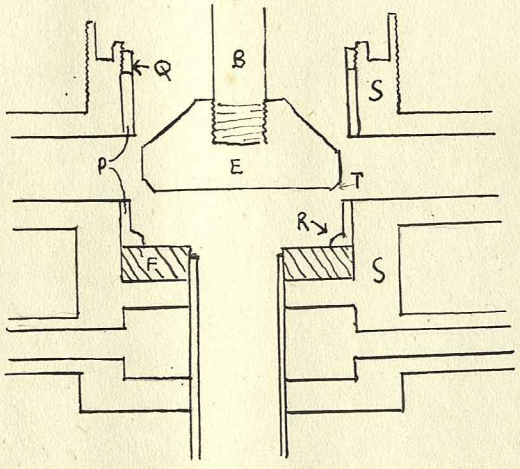
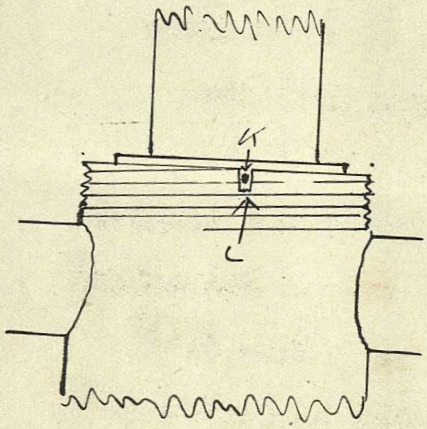


Fig. 2·14

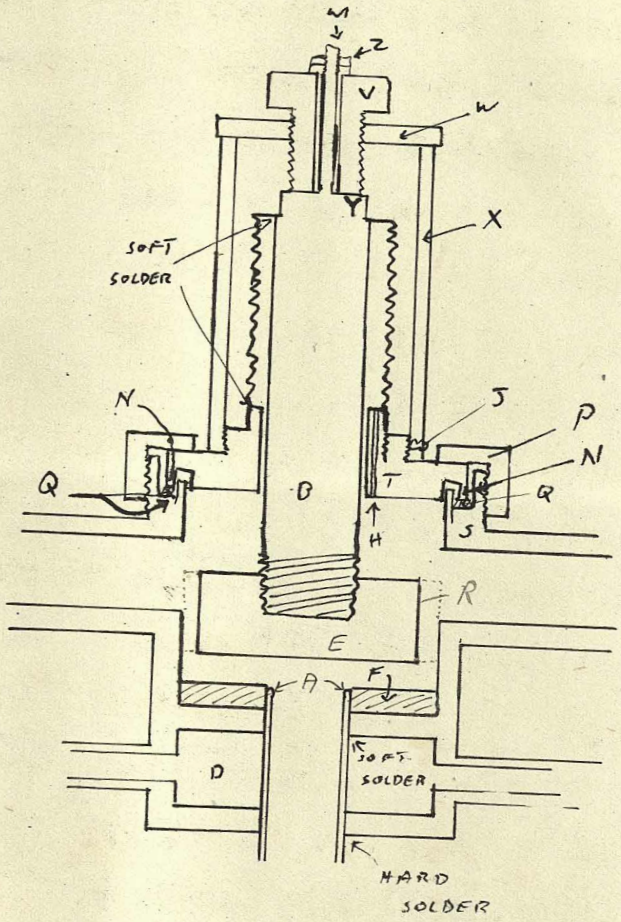
Figure 2·13

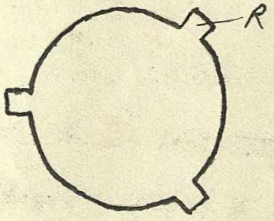


c.



b.





a

we were dealing with trapped air rather than a leak, and in that case it could not be in threads, etc., since it was immediately evolved on opening the valve. Now the space X vanishes on opening the valve, but if air were trapped here, it meant that either C and F were not sealing, or D was not closing the space between C and E. Of these the former is most likely, and could doubtless have been overcome by decreasing the thickness of E, but the value would have been very critical, which would have led to mechanical difficulties in production and use, and it was decided to eliminate X by removing the rubber ring D and making the lower faces of C and E flush, as in figure 2.12. (NB: The close resemblance to the valve in figure 2.6). A large leak across was found, however, without doubt due to lack of a seal between C and E (previously provided by rubber between B and E.) This meant however that F was still not sealing at the junction between E and the nickel tube, i.e. the junction Q between C and E was too near the nickel tube. Therefore E must have a considerably larger diameter than the tube, and the plunger shown in figure 2.13, consisting of an aluminium block E screwed directly on B was tested. In this case no groove was cut on E, but a more powerful tightening mechaism was fitted in place of the hand screw used previously, consisting a 3/8" hexagonal bolt V, threaded on the plate W which was hard soldered to the

/valve

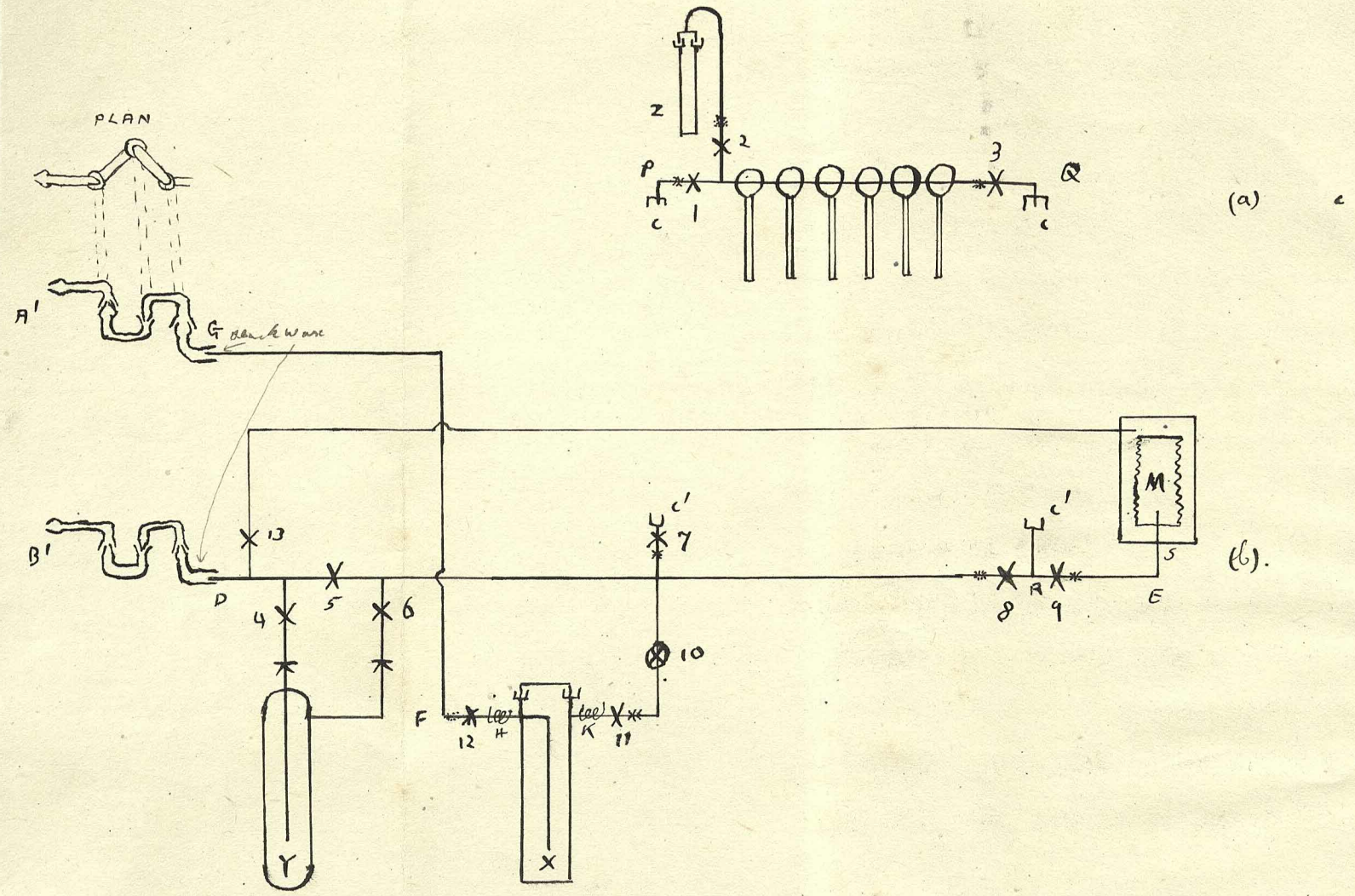


Figure 2·15

✕ = isolation valve

✕✳ .. .. with tailpiece on the same side as the asterisk

⊗ Fine control valve

⋀ Coppergless seal

⊔ Flange & groove joint (soft soldered)

valve casing X. To close the valve, pressure was applied to the shoulder Y, and to open ,to the locking nuts Z on M, a small diameter projection of B passing through V. The cover T (to which the bellows was soft soldered) was sealed to the valve body S, by the flange N fitting in the groove Q containing a rubber ring, pressure being applied by the brass ring P tightened by a C-spanner.

To prevent E having several grooves cut in it, by sideplay of B, it was centralised by three ribs R (figure 2.13a) which were a sliding fit in S, and B was a sliding fit in T (Three vents H were therefore provided to evacuate the bellows). Also, a pin K (figure 2.13b) on T fitted in a slot L in S to prevent the valve top (and with it E) rotating when P was tightened. A grub screw J prevented X from rotating as V was tightened.

D was a water jacket cut from the same block as the valve body, which was more efficient than a copper spiral.

This valve was quite leak proof and remained so after several weeks' operation with hex, and it was decided to use it in the full scale apparatus, shown diagrammatically in figure 2.15a. During construction however a slight alteration was made in the plunger as in figure 2.13c which was, in my opinion, undesirable, as it meant that the thrust was transmitted by a small area of brass which increased the tendency to deform

/the

the aluminium. As a result (and partly perhaps of corrosion of the sliding surfaces) in two months one valve had jammed altogether and one was very stiff. Also F was found to stick to E after the action of hex, and so a modified valve was made as in figure 2.14. In this the brass sleeve P, having holes in alignment with the side tubes, is pushed down to F and held down by the threaded ring Q. E and F cannot therefore stick. E and P are prevented from jamming by making E smaller than P, and centralisation is brought about at the moment of closing by the flange R and the bevel T.

(iv) Main Apparatus.

The apparatus finally used consists of a number of detachable sampling units (figure 2.15a) and the hex unit (figure 2.15b) consisting of a main line DE of 3/8" copper tubing, attached at E by a black wax cup to the high pressure arm of a bellows manometer M which can be closed off by valve 9. The low pressure arm may be pumped out through valve 13.

Hex is stored in a copper pot X (with a soft-soldered lid) containing potassium fluoride degassed for 2 days at 100°, and may be let into the apparatus by valve 11 and a fine control valve 10. H and K are water jackets to protect valves 11 and 12. Connection is made with the main hex bottle (figure 2.1) by the valve 12 and the tube FGA', A' being a cone attached

to A in figure 2.1. The apparatus is pumped through the line B'D and valve 5, B' being a cone attached to cone B in figure 2.1. On either side of valve 5 valves 4 and 6 give access to a glass trap Y, attached by copper-glass seals, for the removal and purification of hex. The sampling units are attached by the vac-unions C'. This part of the apparatus is supported by a heavy steel frame, and since the pumping system is supported by the rather more flexible 1/4" gas piping, connection between the two is affected by a system of cones, as shown, which permit free relative motion in the plane of the bench. The junction from glass to copper is here made by black wax.

The sampling units consist of 2, 3 or 6 reaction tube valves, joined by 3/8" copper tubing, ending in two tapered projections C for attachment to the vac-unions C'. The system may be closed to the atmosphere by valves 1 and 3. Z is a 1" diameter nickel tube, soft soldered to a copper tube joined to PQ by valve 2. This is intended for storage of hex for use in long "soaks", in a thermostat.

The asterisks indicate upon which side of the valve the bellows is located, where this is of importance, e.g. valves 11 and 12 have the bellows on the far side from the hex bottle, to prevent hex crystallising in them, which may cause puncturing or sticking. Valves 1, 2 and 8 are as shown in order to make the volume PQRS

Vac

as small as possible for maximum senstivity of the manometer, whilst 3, 7 and 9 are arranged so that when the sampling unit is off the apparatus, and C' exposed to air, the bellows manometer is not exposed. This is to keep the area which might pick up atmospheric water to a minimum.

SECTION III. EXPERIMENTAL PROCEDURE.

(i) The Method.

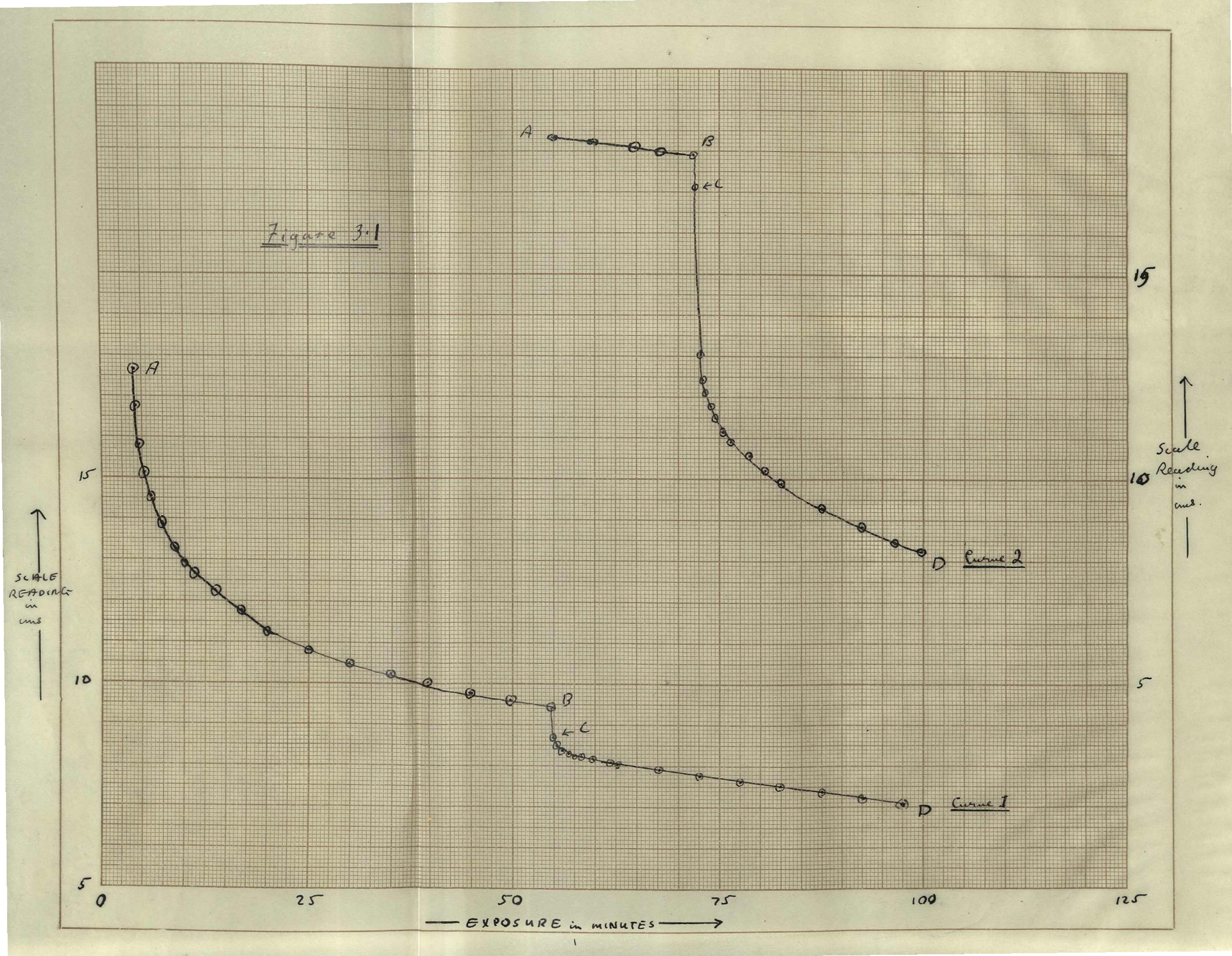
This was to consist essentially of placing membrane material in a vessel which itself had very little reaction with hex, filling with unsaturated hex vapour and measuring the loss of hex by a method based on measurements of pressure by a bellows manometer. A control experiment was to be performed to find the loss of hex in an exactly similar but empty vessel.

On the results of previous work on the reaction of hex with bulk metals, it was decided to use as a reaction vessel a nickel tube closed by a valve, constructed in such a manner, that, when closed, only aluminium and nickel were exposed to the hex in the tube. The development of this valve was described in Section II.

For the measurement of pressure, hex was to be expanded into a bellows manometer and then returned to the nickel tube by condensation.

Using this method, Dr. G. O. JOnes (Oxford Report No. 44, page 23) had shown that errors due to losses of hex in the connecting tubes and manometer could be eliminated by the method described here. When hex vapour is first placed in the system there is a large rapid pressure fall which gradually decreases in rate. After about 15 minutes, the rate becomes constant and of such a low magnitude (0.2 mms. Hg. per

/hour


Figure 3.1
A
B
C
D
Curve 2
A
B
C
D
Curve 1
15
10
5
0
25
50
75
100
125
SCALE READING in cms
Scale Reading in cms.
EXPOSURE in MINUTES

hour) that during the time required to measure the pressure and condense the hex, the loss is too low to be observed. This is illustrated graphically by the portion AB of curves 1 and 2 (figure 3.1). It was found that the degree of stability in the manometer and connecting tubes was not decreased by pumping for any period less than 15 minutes, but that pumping overnight rendered fresh stabilisation necessary.

Having thus temporarily stabilised the manometer system, the reaction tube valve was opened, and after a pressure drop BC, due to the change in volume, curves CD of the same form were obtained for the newly exposed surfaces. Curve 1 is for the blank vessel, curve 2 for the membrane container. The final slope in the former case is the same as for the manometer system, i.e. the loss in the tube alone is not measurable in such a short time. The loss in the membrane tube is naturally much larger.

When a steady fall had again been reached, the hex was purified as described below (paragraph iic), and the pressure measured at room temperature. It was then condensed into the tube by a suspension of finely powdered solid carbon dioxide in alcohol (-80°C), and the pressure again read. Finally, complete condensation was effected by liquid air, and the valve

/closed.

closed. The temperature of the tube was then raised to the required value by a copper-tube electric furnace of about 2" diameter which gave very uniform heating.

Then if p_1 = the pressure at room temperature

p_2 = the pressure at -80°

p_3 = the pressure at liquid air temperature

$x(p_1 - p_2)$ = the pressure of hex in the tube

$x(p_2 - p_3)$ = the pressure of hydrogen fluoride in the tube,

where x is a factor depending on the relative volumes of the tube, and the manometer system.

It is assumed that hex and hydrogen fluoride do not associate in the vapour phase.

At the end of a given period the manometer system was again stabilised and the contents of the reaction tube analysed by taking the pressures at liquid air temperature, -80° and 20°. Hence, from the amount of hex in the tube initially and finally the loss in the given period was known. The period of the test was always limited so that the fall in pressure never exceeded 20% of the initial pressure. This was to limit possible effects due to changes in reaction mechanism or adsorption brought about by pressure changes. Further, by ensuring that there was a sufficient quantity of hex left at the end of a test, it was certain that reaction had proceeded as far as it could, i.e. low values for the uptake, by reason of lack of reactant, were avoided.

/for

For each period the consumption in the "blank" tube was subtracted from that in the membrane container and the uptake in the membrane found. Then a consumption-time curve was drawn by adding all the separate lossses and the corresponding times. Such curves are discussed in Section IV. It should be observed that although they are drawn continuously these curves consist of two parts, that for the first half hour or so being obtained at a pressure of about 1.7 mm. mercury and the remainder at about 33 mm. mercury. There is no evidence for believing that the reaction is in any way different at these two pressures.

(ii) Justification of the Method.

(a) Uptake by the apparatus.

Experiments in the preliminary apparatus showed that the uptake in the "blank" tube was very much less than that on even a small quantity of membrane, and this is clearly illustrated by curves 1 and 2 of figure 4.1, taken from results on the main apparatus.

Curve 1 for the "blank" tube represents an uptake of 0.7 mgm. hex in 5 days, with a final slope of 0.05 mgms. per day.

Curve 2 for forty square centimetres of nickel membrane represents an uptake of 15.7mgm. in five days with a final slope of 0.8 mgms. per day.

In cases where it was found that stabilisation of the membrane had reduced its rate of uptake to values of the same order as that of the "blank", the experiment

/was

was repeated with a larger area of membrane.

(b) Valve Efficiency.

Periodically throughout a series of experiments, dry air was let into the apparatus to a pressure about 5% greater than that of the hex in the tube, for several hours. Then if a leak had developed across the valve it would immediately have been obvious on analysis by the pressure (p_3 above) at liquid air temperature.

No such leak has been found after three months continuous work. Further, no points had been found to be off the curve, due to leaks across, or indeed from any other cause.

(c) Hex Purity.

According to W. J. SKinner, (of I.C.I. Billingham) "A Preliminary Study of the Removal of HF from VI", November, 1943, hex and hydrogen fluoride form a constant evaporation mixture containing 2 mol percent of hydrogen fluoride at 0°C. This purity can be obtained by repeated sublimation at -80°C, with pumping. Purity greater than this can only be obtained by standing over solid anhydrous potassium fluoride. Accordingly the hex container (X, figure 2.1) was filled with degassed potassium fluoride, and all experiments performed with hex from this supply.

During the preliminary pressure fall in the apparatus, some hydrogen fluoride is formed, probably by reaction with water vapour and this is undoubtedly adsorbed by the walls (which are coated with copper fluoride). A similar reaction

/probably

probably occurs during an exposure in the reaction tube, and therefore before finally condensing hex into the tube, it was purified by pumping at -80°C, at which temperature hydrogen fluoride has a vapour pressure of 5 mms. mercury.

The condensation-pump-expansion cycle was repeated until a constant pressure 0.01 mms. mercury was reached, at -80°C. A further expansion was then made to ensure that no loss had occurred since the previous measurement, and to ensure also that no vapour had been attracted from the walls of the apparatus by the application of low temperatures, i.e. the expansion-condensation process is reversible and may be repeated several times. This is a striking demonstration of the results mentioned in paragraph (i) above.

Last traces of hex were condensed by liquid air and the valve quickly closed to avoid distillation of hydrogen fluoride into the tube from the walls of the connecting tubes.

During all experiments, the initial condensation was brought about with the low temperature bath covering the lower inch of the tube only, so that when pumping the -80° bath could be raised well above the level of hex in the tube to prevent evporation due to heat conduction down the tube.

When analysing the contents of the reaction tube after a test, hydrogen fluoride was never pumped off before

/the

the hex pressure had been measured at room temperature, since it would have carried some hex away with it.

(iii) Precautions.

(a) The possibility of hex adsorption.

If hex is adsorbed on treated membrane or the walls of the apparatus, two distinct errors may be introduced.

1. The uptake during the first half hour or so was always measured by finding the total pressure drop, and this was obviously equal to the sum of the losses due to adsorption and reaction. It is therefore necessary to examine the membrane for adsorbed gas at the end of the half hour. This has not yet been done. On the other hand examination has been made at the end of several days' exposure (Experiment A below) and the amount of adsorbed hex was found to be small, and probably zero. Therefore if adsorption occurs in the first half hour, it is followed by slow reaction. It is hoped to examine this question in the near future, but until it is done it will be assumed that the pressure drop in the first half hour is entirely due to reaction.

2. The uptake for the remaining periods was measured as the difference between two hex pressures, each in equilibrium with membrane. Hence an error would occur only by virtue of the change in adsorption due to the change in pressure during a test period. This was shown

/to

to be negligible, (Experiment B below).

Two tests were made.

A. At the end of experiment 3, section IV, a test was made to find if any vapour could be distilled from the membrane into a tube cooled in liquid air, and if so its nature. A control experiment was performed to find the corresponding fact about the tubing and manometer. It was found that the connecting tubes yielded hydrogen fluoride and no measurable amount of hex, and the membrane yielded a large amount of hydrogen fluoride and probably no hex; certainly very little.

All hex was removed to Y, and the apparatus pumped for three minutes. The membrane tube and valve 5 (figure 2.15) were then closed and liquid air placed round the "blank" tube for thirty minutes, at the end of which time the temperature of the tube was raised to -80°C.

The pressure rose quickly to 0.07 mms. mercury, and then slowly fell. When it reached 0.03 mms., the bath was replaced by water. The fall continued without change.

Therefore hydrogen fluoride only was evolved by the walls and was quickly re-adsorbed.

The apparatus was then treated with hex for ten minutes to stabilise and pumped for one minute.

Liquid air was placed round the "blank" tube and

/the

the membrane tube opened and raised to 50°C. After twenty minutes it was closed again, and the "blank" tube raised to -80°C.

The pressure rose to 0.7 mms. mercury and fell in three minutes to 0.3 mms. mercury when the temperature was raised to 20° by a water bath. An immediate rise of 0.05 mms. was observed, and then the fall continued. This rise is easily accounted for by thermal expansion, and therefore it was concluded that only hydrogen fluoride is evolved from the membrane after long hex treatment.

B. At the end of experiment 2, section IV, a test was made to observe directly any change in adsorption of hex on a treated membrane, with change in pressure. No measurable adsorption was found. For this purpose the membrane was pumped for one minute, pure hex put in the tube and the valve closed. The "blank" tube was pumped for five minutes and closed. The hex in the membrane tube was expanded and the usual steady fall observed. The hex was then condensed into the "blank" tube by liquid air, for five minutes. The membrane was then shut off and the hex expanded. Exactly the same pressure was observed as when it had been in contact with the membrane. Experiment A showed that if hydrogen fluoride had been evolved from the membrane, it would have been re-adsorbed by the walls, and so it was concluded again that no hex adsorption occurs.

/(b)

TABLE IV.

Blank tube		Reaction tube				
Total exposure	Total hex loss mgm.	Total exposure	Total hex loss mgm.	Loss in blank tube in same time mgm.	Loss in membrane mgm.	
1	2	3	4	5	6	
15 min.	0.15	15 min.	3.79	0.15	3.64	at 1.7 mm.
45 min.	0.15	37 min.	4.59	0.15	4.44	
4 hrs.	0.22	2 hrs.	6.36	0.19	6.17	at 33 mm.
9½hrs.	0.32	4 hrs.	7.82	0.22	7.60	
21 hrs.	0.42	9 hrs.	9.37	0.32	9.05	
45 hrs.	0.54	20⅓ hrs.	10.98	0.42	10.56	
116 hrs.	0.64	44 hrs.	13.00	0.53	12.47	
118¾hrs.	0.69	114¾ hrs.	16.15	0.63	15.52	
		117¼ hrs.	16.23	0.68	15.55	

(b) Hydrogen Fluoride Adsorption.

Experiment A of paragraph (iii)(a), above, showed clearly that hydrogen fluoride is adsorbed on the walls and could be pumped off. But when purifying hex a large pressure of hydrogen fluoride was often observed indicating that the walls may become effectively saturated. If the apparatus were pumped and the pumps shut off a pressure of 0.01 mm. mercury was quickly built up, but not exceeded,

1. in the manometer and connecting tubes, or
2. over hex at -80°, or
3. over treated membrane either at 20° or 50°.

There therefore appears to be an equilibrium pressure of 1×10^{-2} mm. mercury over the metallic fluorides on the walls, and so pumping hex at -80° will not purify it further than this. All hex used in the experiments was therefore of a standard purity, so long as the walls were thoroughly pumped.

Now it was assumed that this pressure over hex at -80° was due to hydrogen fluoride alone, but it may also be due partly to hex. The error introduced however will be small, less than 0.01 mm. ercury.

Similarly, the error introduced by warming this small quantity of hydrogen fluoride from -80° to 20° will be negligible.

(c) Vacuum Effect.

It has already been stated (paragraph (i) above)

/that

that pumping for a few minutes does not decrease the stability of the walls of the apparatus after hex treatment, and the non-evolution of gas from membrane into the closed and evacuated containing tube, above the equilibrium pressure of 0.01 mm. (test 3, paragraph (b) above) seems to indicate a similar state for treated membrane. On the other hand at the end of experiment 5, section IV the membrane was pumped for 24 hours and tests continued. Renewed activity was observed. It was therefore decided that at no time during a continuous series of tests, must a tube be left empty for any length of time. Even liquid air may cause the same effect by distillation to the bottom of the tube.

(d) Temperature Correction.

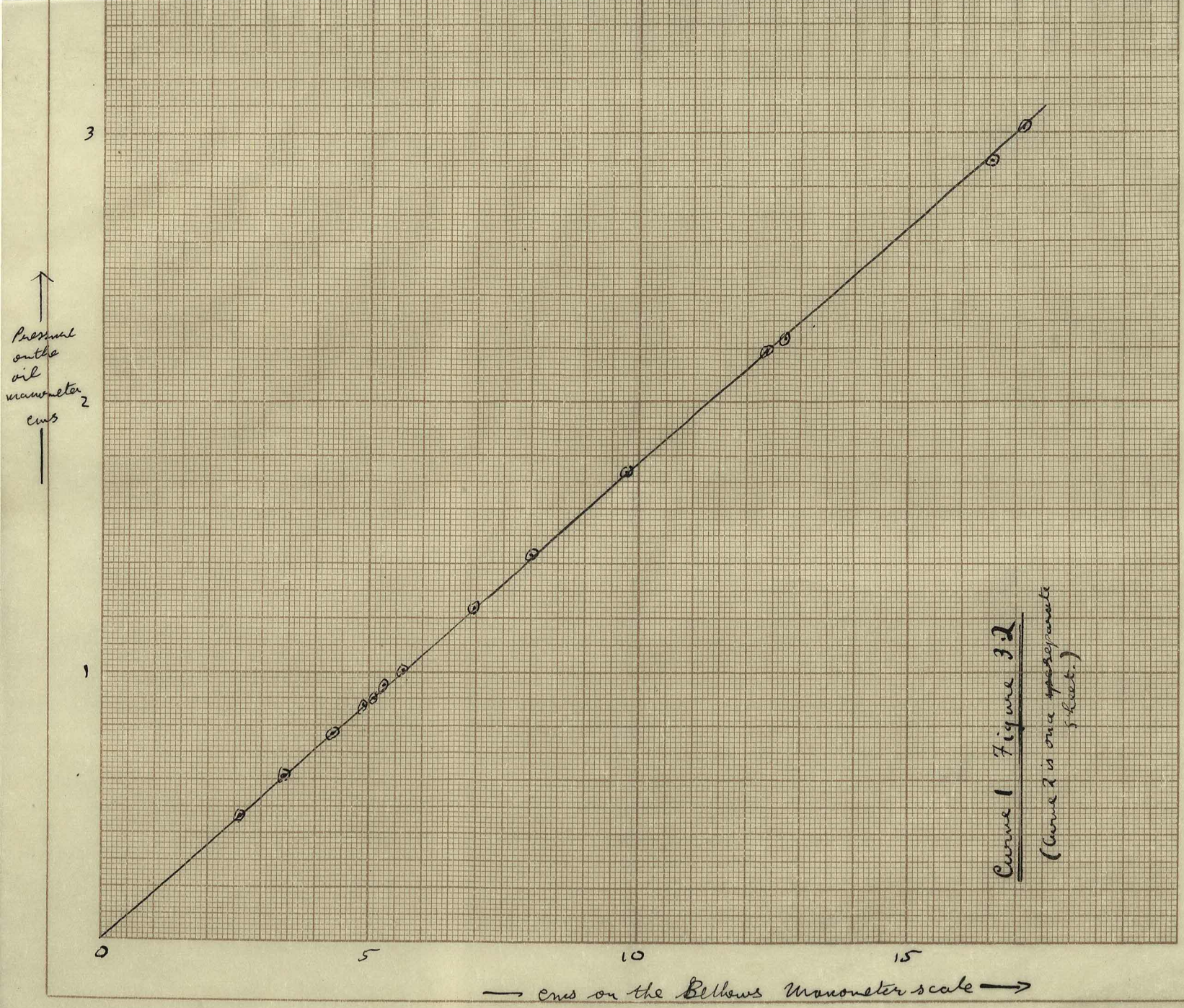
It was noticed that room temperature varied over a range of 5°C and therefore all measurements of hex pressure were corrected to 20°C, the temperature of the gas at the time of measurement being taken as that recorded by a thermometer placed near the manometer.

(iv) Sensitivity and Calibration.

(a) Calibration of the manometer.

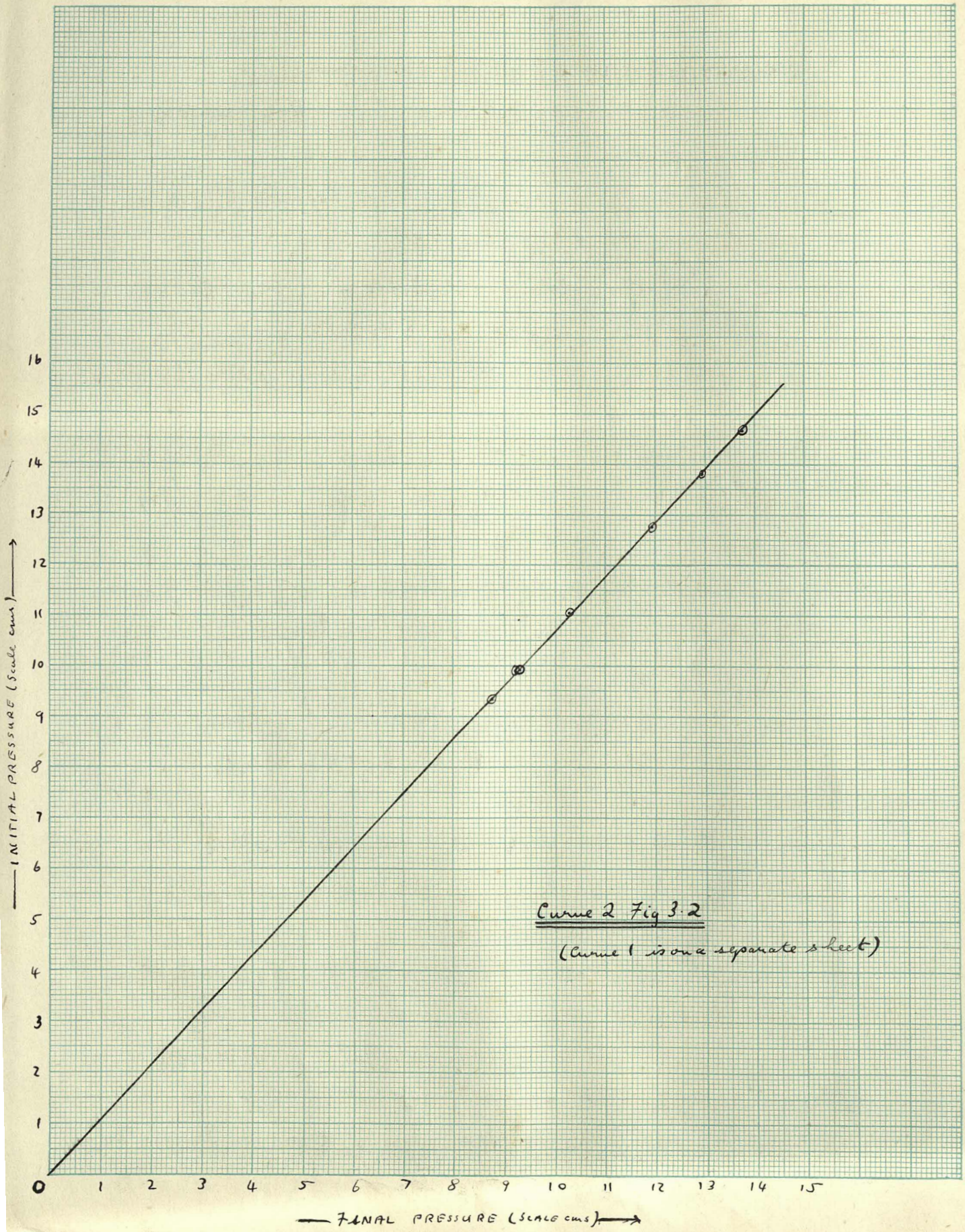
The manometer was calibrated by measuring the deflection due to a quantity of dry air in temperature equilibrium with the room, (obtained from the flask S, figure 2.1) and with the liquid air trap shut off, whose

/pressure



Curve 1 Figure 32

(Curve 2 is on a separate sheet.)



Curve 2 Fig 3.2

(Curve 1 is on a separate sheet)

pressure was read off on the oil manometer M.

Curve 1, figure 3.2 is a plot of the deflection in cms. against pressure in cms. of oil.

Hence from a knowledge of the density of oil at the temperature of the experiment,

1 cm. scale deflection = 0.11 mm. mercury.

(b) The volume of the manometer system.

The volume of hex in the manometer system during each measurement was found in two ways.

1) The reaction tube was filled with dry air at a pressure measured on the oil manometer and the valve closed.

The apparatus was evacuated and the air in the tube expanded into the manometer system and the scale reading noted.

This reading was converted to its equivalent on the oil manometer by the calibration curve, and the volume ratio found.

2) The apparatus was pumped and the reaction tube closed. Dry air was let into the manometer system and its pressure measured.

The reaction tube was opened and the pressure again measured. Hence the volume ratio.

This method is exactly analogous to that used for the measurement of the first uptake of hex on membrane. The results are given in curve 2, figure 3.2.

The volume of the reaction tube being known from

/its

its dimensions, the volume of hex measured may be found and from that the weight of hex corresponding to 1 cm. on the bellows manometer scale.

In all the experiments described in Section IV in which valves 1, 3, 7, 8 and 9 were open. 1 cm. on the bellows manometer scale ≡ 0.48_6 mgm. hex.

NOTE. Method 1 gives the ratio of the volume of the tube to that of the manometer system with the reaction-tube <u>open</u>, and this is therefore the correct ratio to use in finding the weight of hex present from its pressure.

Method 2 gives the ratio of the volume of the tube to that of the system, with the valve <u>closed</u>. The difference (about 6%) can be explained by assuming a volume change of 0.8cc on opening or closing the valve, which is within the bounds of possibility. Since, however this method corresponds to the procedure in admitting hex to the membrane initially, curve 2, figure 3.2 was used to find the drop due to expansion (CB in curves 1 and 2, figure 3.1) when calculating the initial uptake. (See also column 2 of Table I, Section IV and the accompanying explanation.)

(c) <u>Sensitivity</u>.

The manometer was illuminated by a line filament lamp, an image of which was thrown upon a ground glass scale by a lens. The image was about 1 mm. in width, being slightly broadened by vibration.

/It

It is estimated that this could be read to ± 0.5 mm. only.

Allowing a further 0.5 mm. for uncertainty in applying corrections for the effects described in paragraph (iii)(b) above, the measurements may be assumed accurate to ± 1.0 mm. on the scale, which is equivalent to 0.01 mm. of mercury, which is 0.67% at the pressures usually used (1.7 mm. of mercury).

Then the amount of hex taken up may be measured to within ± 0.05 mgm.

SECTION IV RESULTS.

(1) Note on placing membrane in the reaction tube, and removing it.

In each of the experiments about to be described the following procedure was observed when filling a tube with membrane.

A measured area of membrane was cut into narrow strips not longer than 8 cms., and the strips packed into one end of a brass tube whose external diameter was just less than the internal diameter of the reaction tube.

Dry air was admitted to the reaction tube to one atmosphere pressure and valves 1 and 3 closed (figure 2.15).

The valve top on the reaction tube was removed and the brass tube containing membrane inserted until it reached the bottom, and the membrane was pushed out by a plunger fitting in the brass tube. The object of this was to ensure that the membrane was all at the bottom of the reaction tube with a clearance of 2 cms. between it and the water cooler, and to minimise the risk of leaving small particles of membrane on the polished edge of the nickel tube, which would eventually ruin the plunger.

After brushing the upper edge of the nickel tube with cotton wool the valve top was replaced, and the apparatus evacuated. This was done as soon as possible after opening, to reduce the amount of atmospheric air entering the apparatus by diffusion.

/The

The membrane and blank were then degassed above room temperature and the exposure begun.

Before removing membrane at the end of an experiment, it was degassed at 200° for about 12 hours before opening the tube, to decrease reaction between hex and atmospheric water, a little of which cannot be prevented from entering, and then dry air let in to one atmosphere.

Valves 7 and 8 were then closed (9 being already closed), the valve top removed, and the sampling unit detached from the base for as short a time as possible, and inverted. The membrane fell out quite easily and the number of strips was checked to ensure that none were left in the tube.

(ii) Results.

The General Method of measuring the hex consumption has already been described (paragraph (i) Section III) and the following tables give values of uptake (in mgm.) only, except in the case of Experiment 1, where all relevant readings (in scale units) are also given, to indicate precisely how the results were calculated.

The milligram, rather than the milligram per square foot was taken as the unit when plotting the results since it was desired to compare the uptake on the membrane with that in the blank tube. For convenience each graph has been marked with one reading in milligrams per square foot.

All the experiments were done with the same area of

/membrane

membrane, except the fifth, for which a subsidiary plot has been made showing the equivalent uptake on 2/7 of the area used, so that the graphs for all five experiments can be compared directly.

It will be seen from Tables II and III that the hydrogen fluoride pressure during Experiment 1 was at all times about 2 mm. on the scale. This applies to all the experiments, and since (as explained in paragraph (iii) (b) of Section III) these pressures bear no relation to the amount of hydrogen fluoride formed, they will be omitted in the remainder of the results.

Note. The membrane used in experiments 2-5 is referred to for brevity as J23 or J41 membrane.

J23 was made from Mond Nickel powder, size 2.7μ, sintered at 800° and rolled from a thickness of 10 mil to one of 3 mil.

γ_0 lies between 1 and 2 x 10^{-3}

G lies between 2.3 and 2.8.

J41, the membrane used in Experiment 5 is also made from Mond Nickel powder, but 4.5μ in size, sintered at 970° and rolled from 12.5 to 7 mil.

γ_0 is about 10 x 10^{-3}

G lies between 5 and 6.

Experiment 1.

To measure the uptake on 40.5 sq. cms. of J23 membrane at 50°C.

Degassing: 40 hours at 100°.

The

TABLE I.

1	2	3	4	5	6	
Pressure of hex at the time of opening the tube. Scale cms.	Drop due to the volume change. Scale cms.	Time of each exposure Minutes.	Measured Pressure Fall. Scale cms.	Calculated pressure fall in the tubing in the same time Scale cms.	Pressure fall in blank tube alone. Scale cms.	
13.55	0.85	15	1.60	0.45	0.30	Blank
-	-	22	0.65	0.66	0.01	
-	-	8	0.24	0.24	0.00	
13.25	0.80	15	9.05	0.45	7.80	Reactio tube
14.05	0.85	22	3.15	0.66	1.64	

TABLE II.

Pressures recorded when hex was put into the tube before exposure in Scale cms.								Pressures recorded when the hex was analysed after exposure in scale cm.s								
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
The tube -180° (zero)	The tube -80°	The tube room temp.	Room temperature °C	HF present as gas	Hex present	Hex corr. to 20°	Time of each exposure hrs.	The tube -180° (zero)	The tube -80°	The tube room temp.	Room temp. °C	HF present as gas.	Hex present	Hex corr. to 20°	Apparent formation of HF cms.	Hex loss in each exposure Scale cms.
2.00	2.10	16.25	20	0.10	14.15	14.15	3¼	2.00	2.30	16.30	20	0.30	14.00	14.00	0.20	0.15
2.00	2.15	15.70	20	0.15	13.55	13.55	5½	1.95	2.10	15.50	19	0.15	13.40	13.35	0.00	0.20
2.00	2.15	15.55	19	0.15	13.40	13.35	11½	2.00	2.30	15.30	17	0.30	13.00	13.15	0.15	0.20
2.00	2.10	14.85	17	0.10	12.75	12.90	24	1.95	2.10	14.60	17	0.15	12.50	12.65	-0.05	0.25
2.00	2.15	14.25	17	0.15	12.10	12.20	71	2.00	2.20	14.30	23	0.20	12.10	12.00	0.05	0.20
2.00	2.15	14.00	23	0.15	11.85	11.70	2¾	2.00	2.15	13.75	20	0.15	11.60	11.60	0.00	0.10

T A B L E III.

Pressures recorded when hex was put into the tube before exposure, in Scale cms.								Pressures recorded when the hex was analysed after exposure. in scale cms.								
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
The tube -180° (zero)	The tube -80°	The tube room temp.	Room temp. °C	HF present as gas	Hex present	Hex corr. to 20°	Time of each exposure hrs.	The tube -180° (zero)	The tube -80°	The tube room temp.	Room temp. °C	HF present as gas	Hex present	Hex corr. to 20°	Apparent formation of HF cms.	Hex loss in each exposure Scale cms
0.95	1.10	15.25	20	0.15	14.15	14.15	1 1/4	0.95	1.10	11.60	20	0.15	10.50	10.50	0.00	3.65
0.95	1.05	16.65	20	0.10	15.60	15.60	2 1/4	2.00	2.25	14.85	20	0.25	12.60	12.60	0.15	3.00
2.00	2.10	14.45	20	0.10	12.35	12.35	5	2.00	2.20	11.50	20	0.20	9.30	9.30	0.10	3.05
2.05	2.20	16.60	20	0.15	14.40	14.40	11 1/4	0.95	1.05	11.90	17	0.10	10.85	10.95	-0.05	3.45
0.95	1.10	15.40	17	0.15	14.30	14.45	23 2/3	2.00	2.20	12.40	17	0.20	10.20	10.30	0.05	4.15
2.00	2.15	16.80	17	0.15	14.45	14.60	70 3/4	2.00	2.50	10.70	23	0.50	8.20	8.10	0.35	6.50
2.00	2.15	15.60	23	0.15	13.45	13.30	2 1/2	2.00	2.10	15.30	21	0.10	13.20	13.15	-0.05	0.15

The measurements were obtained in two groups (paragraph (i), Section III), one with hex at 1.7 and the other at 33 mm.

(a) At 1.7 mm.:

Before exposing either the blank tube or the membrane to hex the rate of fall in the manometer system was found to be 0.03 cms. (scale) per minute.

The results for both the blank tube and the reaction tube are given in Table I.

Column 1 gives the pressure of hex in the system at the time of opening the valve, from which the drop due to expansion (column 2) was obtained from curve 2, figure 3.2.

Column 5 was obtained from the rate of fall in the system, (above).

Column 6 is the difference between column 4 and the sum of columns 2 and 5.

(b) At 33 mm.:

Table II gives the observations and losses for the blank tube and Table III those for the reaction tube.

In both cases:

Column 5 is the difference between columns 1 and 2.

Column 6 is the difference between columns 2 and 3.

Column 13 is the difference between columns 9 and 10

Column 14 is the difference between columns 10 and 11

Column 16 is the difference between columns 5 and 13

Column 17 is the difference between columns 7 and 15.

The results are summarised in Table IV, and the uptakes are given in mgm. hex:

Columns 1 and 3 are obtained by summing the separate exposure times in Tables I, II and III.

Columns 2 and 4 are obtained by summing the corresponding losses.

Curve 1, figure 4.1, is a plot of the uptake in the blank tube against time, drawn from the results in columns 1 and 2.

From this curve column 5 was obtained, which gives the uptake in the blank tube in times corresponding to the readings for the reaction tube.

Then the uptake on the membrane alone is the difference between columns 4 and 5 and is given in column 6.

These values are plotted in curve 2, figure 4.1

It should be borne in mind that the values in Table IV are correct to 1% only, and therefore in column 6 the second decimal place is inaccurate.

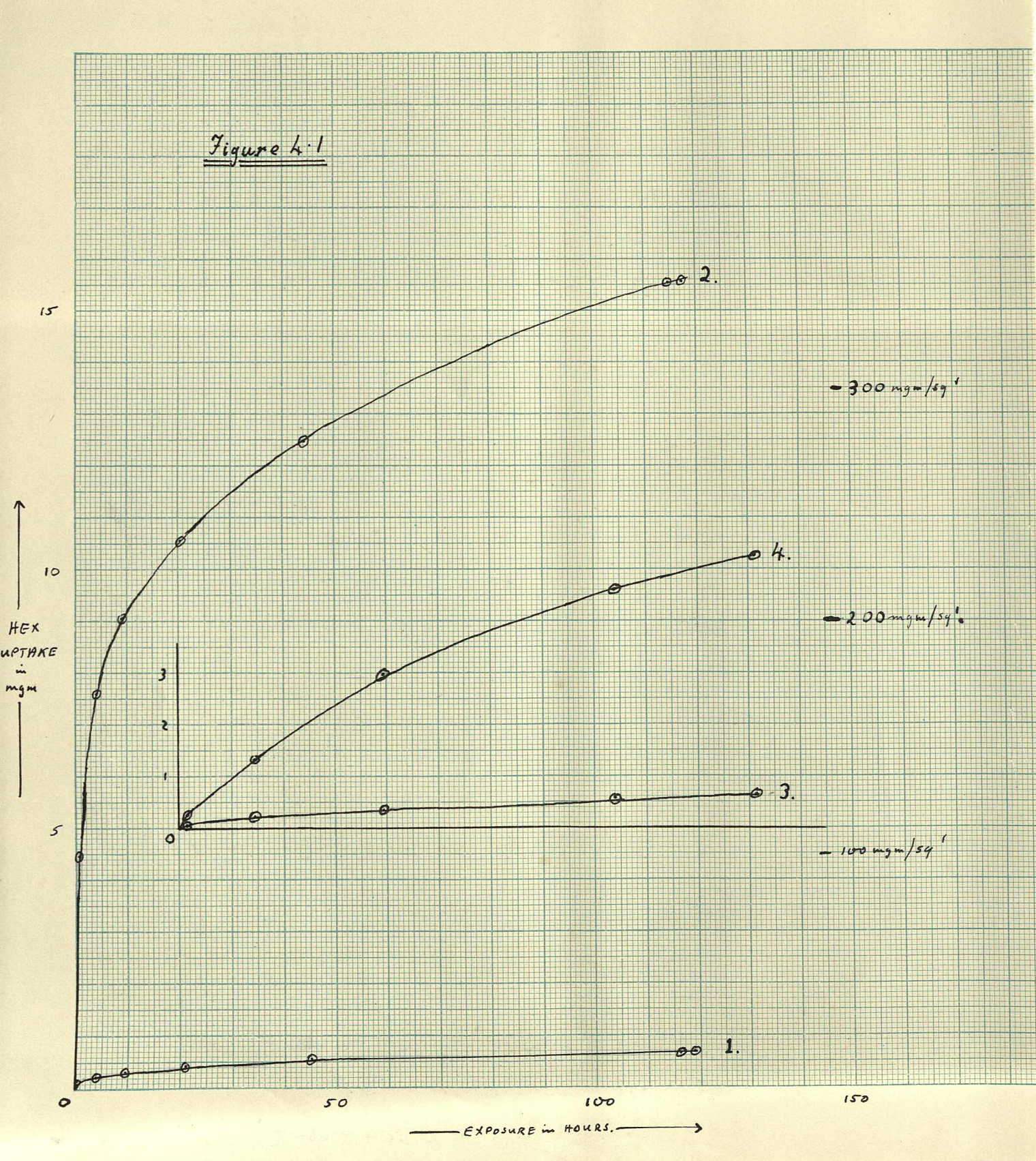
This procedure is involved in all the experiments which follow, but in these the details will be omitted and only final results, corresponding to Table IV, will be given.

The rate of uptake after 120 hours = 17.7 $\pm$0.8mgm. per sq. foot per day.

Experiment 2.

To measure the uptake on 40.8 sq. cms. J23 membrane

/at


Figure 4.1
15
10
5
0
50
100
150
HEX UPTAKE in mgm
EXPOSURE in HOURS.
2.
4.
3.
1.
300 mgm/sq'
200 mgm/sq'
100 mgm/sq'
3
2
1
0

at 50°C.

Degassing: 46 hours at 100°.

The uptake in the first 20 hours was not measured, as various exposures were made to hex at 80 mm.

The results after 20 hours' exposure, are given in Table V and plotted in curves 3 (for the blank) and 4 (the membrane), figure 4.1, for comparison with the curves of Experiment 1.

TABLE V.

Total exposure hours.	Loss in the blank tube mgm.	Loss in the membrane mgm.	
1½	0.07	0.24	At 33 mm.
14½	0.21	1.31	
39½	0.34	2.99	
84	0.58	4.60	
111¼	0.63	5.26	

The rate of uptake after 120 hours

= 14.0 ± 0.7 mgm. per square foot per day.

Experiment 3.

To measure the uptake on 40.8 sq. cms. of oxidised J23 membrane at 50°.

Oxidation: 3 hours at 300° in atmospheric air.

Degassing: 41½ hours at 300°.

The first 2 minutes of uptake were not measured.

Table VI gives the results obtained and a plot is given in curve 2, figure 4.2 (curve 1 for the blank)

Figure 4.2

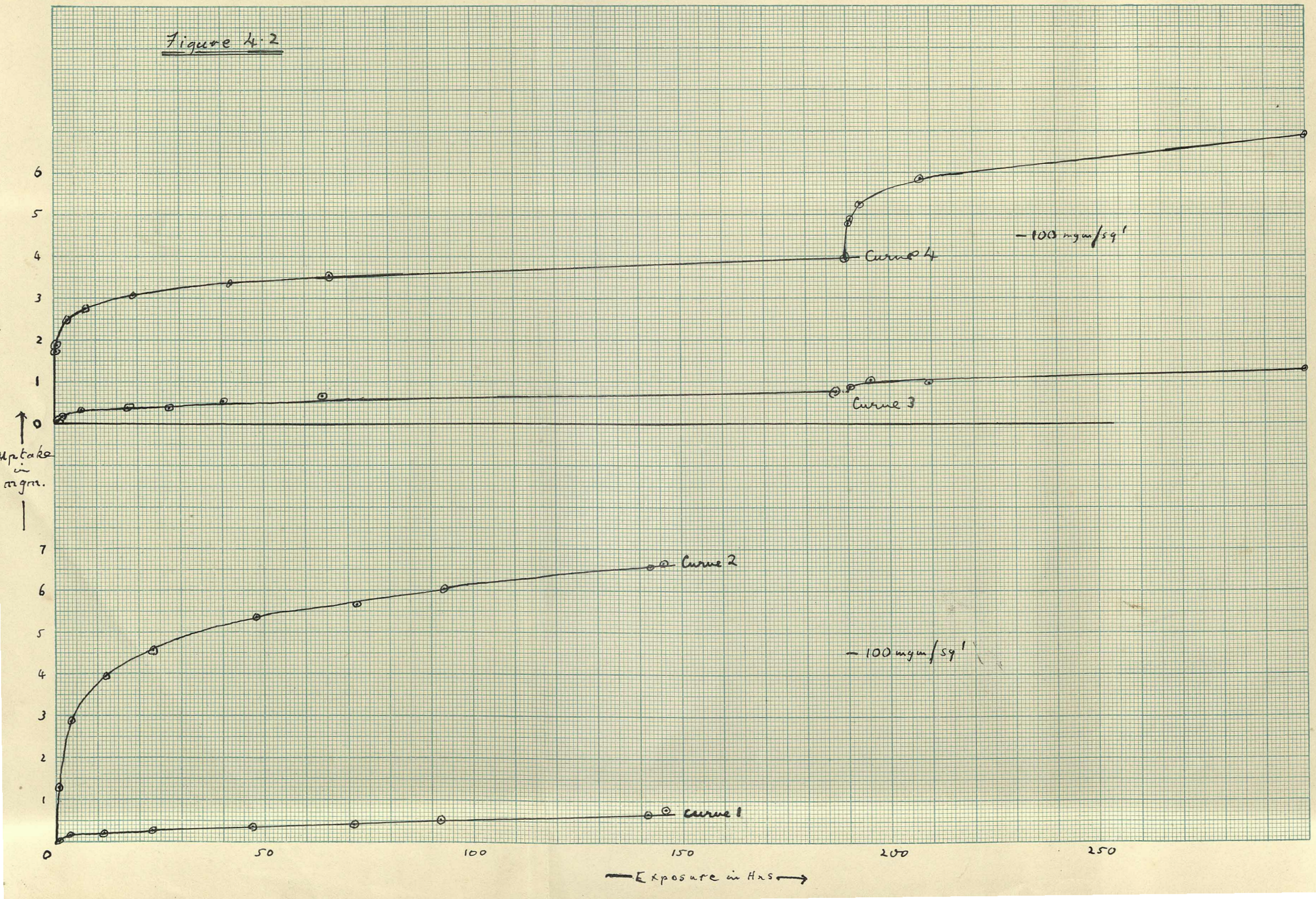

Curve 4
100 mgm/sq'
Curve 3
Curve 2
100 mgm/sq'
Curve 1
Uptake in mgm.
Exposure in Hrs
0
50
100
150
200
250
1
2
3
4
5
6
7

TABLE VI.

BLANK TUBE		MEMBRANE		
Total exposure hours.	Total uptake. mgm.	Total exposure hours.	Total uptake mgm.	
1/4	0	1/2	1.30	at 1.7 mm.
3 1/4	0.15	3 1/2	2.87	
11 1/2	0.20	12	3.96	
23	0.27	23 1/4	4.57	
47	0.37	48	5.38	at
71	0.41	72	5.68	33 mm.
92	0.52	93	6.02	
141 1/2	0.69	142 1/2	6.58	
145 3/4	0.80	145 1/2	6.67	

There was no oxygen found in the tube at any time during this experiment.

The rate of up take after 120 hours=6.6±0.7mgm.per sq.ft. per day.

Experiment 4.

To find the uptake on 4C.8 sq. cms. of oxidised J23 membrane at 50°.

After 190 hours the temperature was raised to 125° and a further series of readings taken.

Oxidation: 3 hours at 300°C in atmospheric air.

Degassing: Very extensive.

The membrane was pumped at a temperature of not less than 50°C for 12 days, for four of which it was 300°C,

/and

and for a few hours 370°.

The results are given in Table VII and curve 4, figure 4.2. Curve 3 is for the blank. Again no oxygen was formed.

TABLE VII.

Blank tube		Membrane		
Total exposure hours	Total loss mgm.	Total exposure hours.	Total loss mgm.	
1/4	0.09	1/4	1.76	at 1.7 mm.
		1/2	1.89	
1 3/4	0.18	3	2.49	at 33 mm.
6 1/2	0.33	7 1/2	2.74	
17 1/2	0.39	19	3.07	
40 1/2	0.53	42	3.36	
64	0.66	65 3/4	3.53	
187	0.76	189 3/4	3.93	

The rate of uptake after 120 hours = 1.9±0.2 mgm per sq. foot per day.

At the end of this series of measurements the membrane and blank (both at 20°) were pumped for 15 minutes, and then for 20 minutes as the temperature rose to 125°. A further set of readings were then taken for the uptake at 125°C. These are given in Table VIII.

/TABLE VIII

TABLE VIII.

Blank tube		Membrane		
Total exposure hours.	Total loss. mgm.	Total exposure hours.	Total loss. mgm.	
1/2	0.12	1/2	0.80	at 1.7 mm.
		3/4	0.95	
6	0.28	3¼	1.34	at 33 mm.
19½	0.24	17¾	1.90	
167	0.71	164¾	3.66	

These results are plotted together with those in the previous table, but the fourth point on the plot was obtained by extrapolation instead of using the value at 164¾ hours.

Experiment 5.

To measure the uptake on 138.5 sq. cms. of oxidised J41 membrane at 50°, after pre-treatment with hex at room temperature.

The measurements were interrupted at the end of 188 hours to investigate the effect of pumping.

Oxidation: (a) Degassing at 20° for 20 hours.

(b) Degassing at 355° for 24 hours.

(c) Oxidation at 315° for 3¼ hours in dry air.

(d) Cool in dry air.

(the

The membrane was exposed to the atmosphere for 1½ hours before placing in the apparatus.

Degassing: 13 hours at 20°.
22 hours at 310°.

Pre-treatment: This consisted in exposure to 80 mm. hex at room temperature for short periods with extensive pumping between each, first at room temperature, and then with the temperature slowly rising, to minimise the risk of reaction between the membrane and hex which may remain.

(i) 5 minute exposure followed by pumping for 11 hours at 20°, and then for 4 hours at 300°.

(ii) 5 minute exposure followed by pumping for 3 hours at 20°, and then for 16½ hours at 330°.

(iii) 10 minute exposure followed by pumping for 2 hours at 20°, and then for 5 hours as the temperature rose to 110°, and then for 16 hours at 110°.

The uptake was then measured and the results are given in table IX. In this case the blank tube was out of order, and so in view of the uniformity so far shown by the uptake in the blank tube, column 2 below was obtained as the mean of all previous uptakes.

The rate of uptake after 120 hours mgm/sq.ft./ day.
= 2.4 ± 0.3.

/Table IX

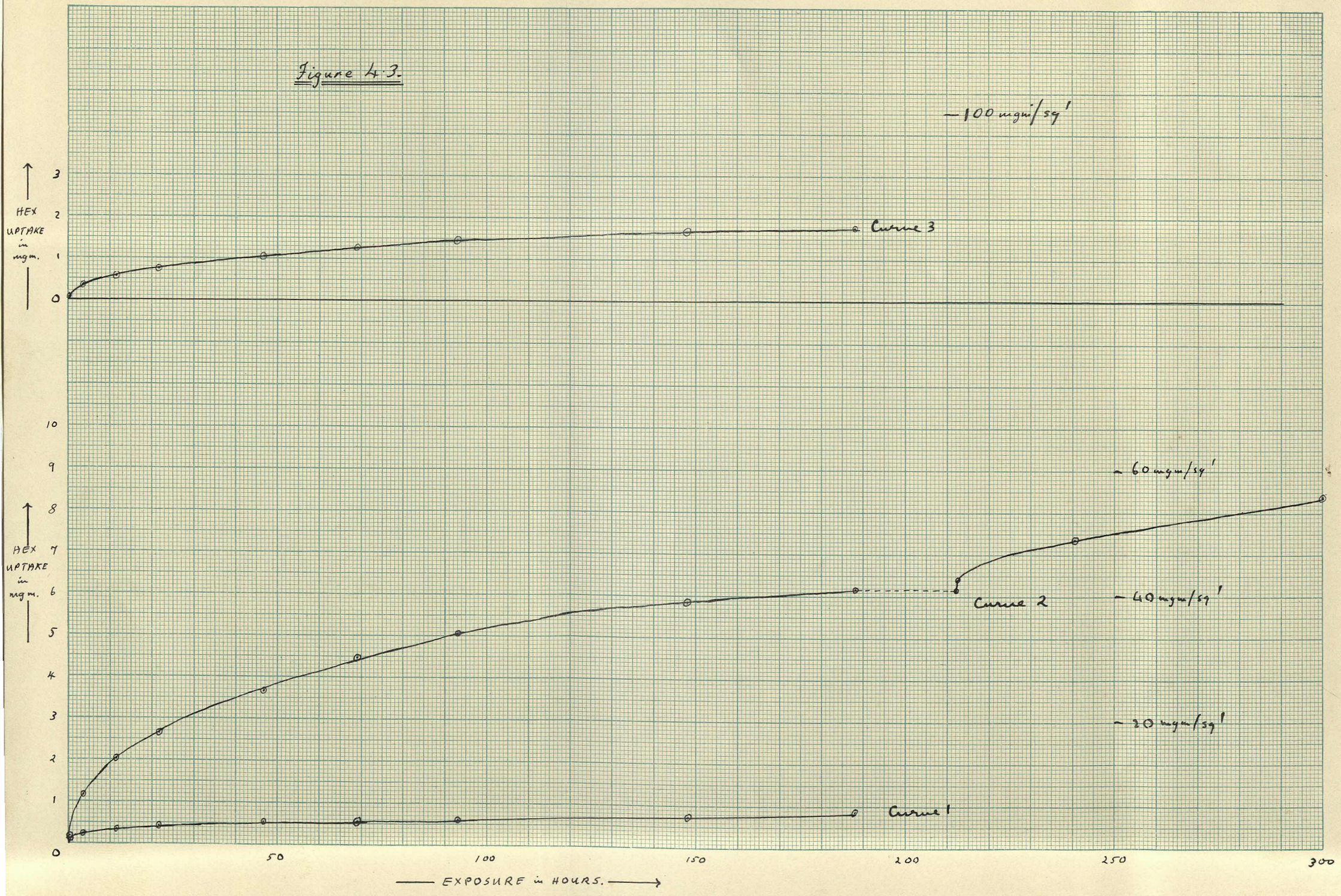
TABLE IX.

Total exposure hours.	Total uptake in blank mgm.	Total uptake on membrane mgm.	Total uptake on membrane ÷ 3.5 mgm.	
1	2	3	4	
1/4	0.11	0.18	0.05	at 1.7 mm.
3 1/2	0.23	1.19	0.34	at 33 mm.
11 1/2	0.33	2.02	0.58	
21 3/4	0.43	2.65	0.76	
46 3/4	0.52	3.65	1.04	
69	0.55	4.48	1.28	
93	0.60	5.06	1.45	
148	0.71	5.83	1.67	
188	0.78	6.17	1.76	
212				
After evacuation 212 1/4		6.40		at 1.7 mm.
After evacuation 240 1/4		7.38		at 33 mm.
After evacuation 352 1/4		9.05		at 33 mm.

At the end of 188 hours' exposure the membrane was pumped at 50° for 24 hours and the uptake again measured. The results are given at the bottom of Table IX (3 readings). No results for the blank tube are available.

/These

Figure 4.3.


HEX UPTAKE in mgm.
3
2
1
0
Curve 3
~100 mgm/sq'
HEX UPTAKE in mgm.
10
9
8
7
6
5
4
3
2
1
0
~60 mgm/sq'
Curve 2
~40 mgm/sq'
~20 mgm/sq'
Curve 1
50
100
150
200
250
300
EXPOSURE in HOURS.

These results are plotted on curve 2, figure 4.3. Curve 1 is for the blank.

The rate of uptake after 120 hours

= 2.4 ± 0.3 mgm. per square foot per day.

The rate of uptake after 190 hours

= 0.9 ± 0.1 mgm per square foot per day.

Curve 3, figure 4.3, is plotted from the values in column 4, Table IX, which were obtained by dividing those in column 3 by 3.5 to obtain the approximate uptake on 40 square centimetres, so that comparison can be made with the curves for experiments 1 to 4.

SECTION V. DISCUSSION.

(I) Justification of the Method.

a) It will be seen that the curves obtained in experiments 1 to 4 are all quite smooth, which indicates that there was no leakage across the valve. This was confirmed by the absence of air in the reaction tube after letting dry air into the connecting tubes. Curve 2, figure 4.3 may have a slight depression between the readings at 46¾ and 69 hours, but if this does represent a leak it was a very small one. There was certainly no leak during the previous period of exposure (21¾ to 46¾ hours, tested by air). It should be noted that this series of results was obtained when the reaction tube valve had shown previous signs of mechanical defect (deformation of the plunger, page 23) from which the succeeding valve should be entirely free.

b) Curves 2 and 4, figure 4.1 show remarkable agreement when it is considered that very small differences in experimental procedure can sometimes cause great difference in behaviour. The membrane in each case was taken from the same sheet.

c) In all cases the curves for the blank tube are given, and the uptake is evidently very much less than that on convenient areas of membrane, from which it follows that the accuracy of uptake measurements is not decreased by uptake on the apparatus. This is in

/direct

direct contrast to the results so far published on the uptake of hex as measured by weighing on a silica spring (page 8) in which no account is taken of the uptake in the spring.

The accuracy in measuring the rates of uptake at the end of long exposures however may be lower, since the slope tends to the same value as that of the blank. This can largely be overcome by using larger areas of membrane. Also, the total consumption per day may become so small that, although the accuracy of a pressure reading is 1% or more, that of the difference between the pressure before and after an exposure unless this lasts several days, is less. It is estimated that an accuracy of 10% for low rates (1-2 mgm./sq.ft./day) is possible.

(ii) Practical Results.

Experiments 1 and 3 show that under the same conditions (of degassing) the uptake on an oxidised membrane is about 50% of that on the untreated membrane for corresponding times of exposure. Now the plugging for untreated nickel (of similar G values, 2.3 - 2.8) at 50° is about 15% in 60 hours, and, if it is assumed that plugging is roughly proportional to uptake in the early stages, the plugging of an oxidised sample would be 7-8%.

In fact, the plugging for membranes of similar G value is not greater than 2% in 60 hours at 50°.

It may be noted in passing that curve 2, figure 4.1 is of the same form as that for the plugging of nickel (at 90°) shown in figure 1·1 (Mr. L. E. J. Roberts).

The curve obtained after very extensive degassing (curve 4, figure 4.2) showed very much better stabilisation and there is little doubt that the removal of water before exposure to hex is a necessary pretreatment.

On the other hand the curve obtained after exposure to hex at room temperature, followed by degassing, figure 4.3, shows no better results than those obtained by extensive degassing alone, and it is still doubtful whether hex pre-treatment has any other value than as a means of removing water quickly and efficiently.

It is evident however that membranes can be produced which have the required maximum uptake (1 mgm./sq.ft./day) or less after exposures lasting about five days.

Uptakes in various times for the separate cases are tabulated below.

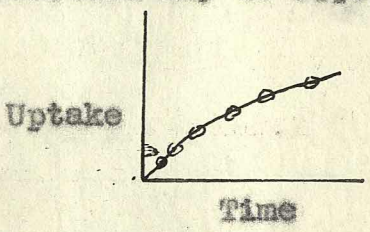
Experiment No.	Type of Membrane	Uptake mgm. after 12 hrs.	60 hrs.	120 hrs.	Rate of uptake after 120 hrs' exposure mgm/sq.ft./day
1	Untreated J23	218	307	359	17·7 ± 0·8
2	Untreated J23				14.6 ± 0.7
3	Oxidised J23	> 90	>126	>147	6.6 ± 0.7
4	Oxidised and very thoroughly degassed J23	66	80.4	86	1·9 ± 0·2
5	Oxidised in dry air and pretreated J41	13.7	27.8	37.1	2.4 ± 0.3

These may be compared with Eduljee's values for an unspecified oxidised Mond nickel membrane at 70° and 80 mm., of 500 mgm/sq.ft. in 2-3 days and a final steady slope of 1.5 - 5 mgm./sq.ft./day.

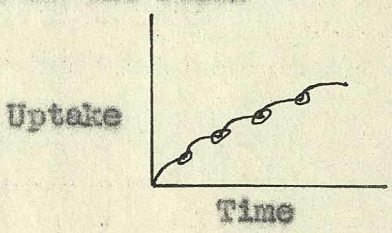
This value for the initial uptake at least is probably far too high.

(iii) The course of the reaction.

a) At the end of long exposures in experiments 1 and 3, short exposures (2-3 hours) were made to show whether the curves were really continuous, or composed of a series of "steps", corresponding to quick reaction in the early part of a single test, followed by a period of comparative inaction until the next test was begun. No evidence of this was obtained, since in both instances these points lie on the curve, i.e the course of the reaction may be represented by curves of the form:



and not



b) It is uncertain as yet whether the inital uptake of hex is due to immediate reaction or physical adsorption. If the latter, then it must be followed by slow reaction, since no hex is adsorbed at the end of an experiment (Experment A, paragraph (iii) a, Section III). Before this can be decided desorption experiments will have to be performed immediately after the initial uptake has occurred.

/Two

Two mechanisms have been suggested for the reaction between metals and hex, both indirect:

1. By the reaction of fluorine from the decomposition of hex according to the equation

$$TF_6 \longrightarrow TF_4 + F_2$$

In this case the American method of stabilisation by fluorination is probably equivalent to a much longer exposure to hex, and stability results from the deposition of a thick layer of nickel fluoride uncontaminated by reaction products such as TO_2F_2.

2. By the reaction of hydrogen fluoride formed from water in the membrane as in the equation

$$TF_6 + 2H_2O = TO_2F_2 + 4HF$$

In this case the layer of nickel fluoride will contain TO_2F_2 and may therefore be less effective in stabilising the membrane, which may account for the large rate of consumption even after 120 hours, on untreated nickel.

In the case of oxidised nickel the reaction may assume a chain form, as

$$TF_6 + 2H_2O = TO_2F_2 + 4HF$$
$$2HF + NiO = NiF_2 + H_2O$$

In this case a layer of fluoride would also be produced, but since it is formed <u>in</u> a layer of oxide already present, contamination by TO_2F_2 may be considerably reduced.

It would still be desirable however to remove most of the water from the membrane to prevent excess of TO_2F_2

/deposited

deposited, and this was found to be so. (Compare curves 2 and 4, figure 4.2).

It is also possible that the difference between the slopes for the lightly and thoroughly degassed specimens is due to water which gradually evolved from the membrane in the former case. If that is so, curve 2, figure 4.2 is the sum of those for two reactions, that with water and that with nickel.

The alternative reaction with nickel oxide

$$TF_6 + 2NiO = TF_4 + 2NiF_2 + O_2$$

seems to be precluded by the absence of oxygen in the reaction tube after exposure (Experiments 3 and 4).

The result of evacuating the membrane for 24 hours at 50° (Experiment 5) has already been mentioned (paragraph (iii)c, Section III). It is of interest in that a definite increase in the rate of uptake was observed as a result of evacuation, and the magnitude of this increase was greater than the uptake would have been if no evacuation had taken place. The reasons for this change, which is of great importance from the point of view of plant work, for it means that a membrane once stabilised may not be exposed to vacuum, are as yet quite unknown but probably depend upon the evolution of hydrogen fluoride, which may cause disruption of the protective layer.

SUMMARY.

(i) The object of this research has been to investigate the possibility of measuring the uptake of hex on membrane material by a method involving pressure fall during reaction, of such a sensitivity that uptakes of the order of one mgm. per square foot per day could be measured conveniently and in a short time. This has been accomplished, and a few exploratory results obtained.

(ii) The main difficulty lay in the design of an isolation valve fitted to a reaction vessel, which was

(a) Quite leak proof, and

(b) Stable towards hex.

The form finally adopted makes the seal by pressing the plane face of an aluminium block firmly against the rounded and polished upper edge of a closed nickel tube (which is the reaction vessel) and eliminating any minute leaks which may remain by causing a rubber ring to press firmly against the line of junction of the nickel and aluminium. This ring was outside the nickel tube and therefore not in contact with hex during an exposure.

(iii) The hex used was of a standard purity (98 mol. percent) obtained by repeated pumping at -80° followed by expansion until a constant vapour pressure at -80° was attained.

(iv) Errors.

1. The possibility of error due to adsorption of hex was investigated and found to be negligible.

/2

2. The uptake of hex on the reaction vessel was reduced to a very low value, and that in the measuring system eliminated entirely.

3. It was found that hydrogen fluoride is adsorbed on the walls of the apparatus and probably an equilibrium pressure is set up. If this is so it is not possible to estimate the exact composition of the vapour over hex at -80°, which may contain hex and hydrogen fluoride. The error introduced is probably less than 1/2% for hex pressure measurements.

(v) Results.

1. The method appears very satisfactory but only one pair of experiments has been performed to test the reproducibility of the results.

The accuracy is probably 1% for measurements of uptake and 10% for measurements of the rate of reaction at the end of an experiment if measured in 1-2 days. For measurements over longer periods the accuracy is greater.

2. The uptake curve for nickel is of the same form as the plugging curves obtained by other methods but direct comparison is not possible since no 50° plugging curves are available.

3. Oxidation of nickel membrane in air at 300° for 3 hours before exposure to hex considerably reduces the rate of attack, and if the membrane is very thoroughly degassed in addition, it has a sufficiently low rate of attack after five days' exposure, to be used in the plant.

/4.

4. The possible mechanism of reaction.

(i) No oxygen is formed during the reaction between hex and oxidised membrane which seems to preclude the possibility of the reaction

$$2NiO + 2TF_6 = 2NiF_2 + 2TF_4 + O_2$$

(ii) Removal of water at the start of the experiment seems to play a very important part in the stabilising treatment, and large quantities of hydrogen fluoride have been found adsorbed on a membrane after exposure, and it is possible that the reaction is due, at least partly, to the chain reaction

$$2H_2O + TF_6 = TO_2F_2 + 4HF$$

$$2NiO + 4HF = 2NiF_2 + 2H_2O$$

PART II.

SUPPLEMENT.

CONTENTS.

		Page.
SECTION I	INTRODUCTION.	1.
SECTION II	RESULTS.	3.
SECTION III	DISCUSSION.	
(i)	"Negative Uptake".	9.
(ii)	General.	12.
SECTION IV	SUMMARY.	14.

NOTE: All curves are numbered in order of appearence in the supplement, preceded by the letter "S". Tables and Experiments are numbered in continuation of the B.A. Thesis (Pt. I).

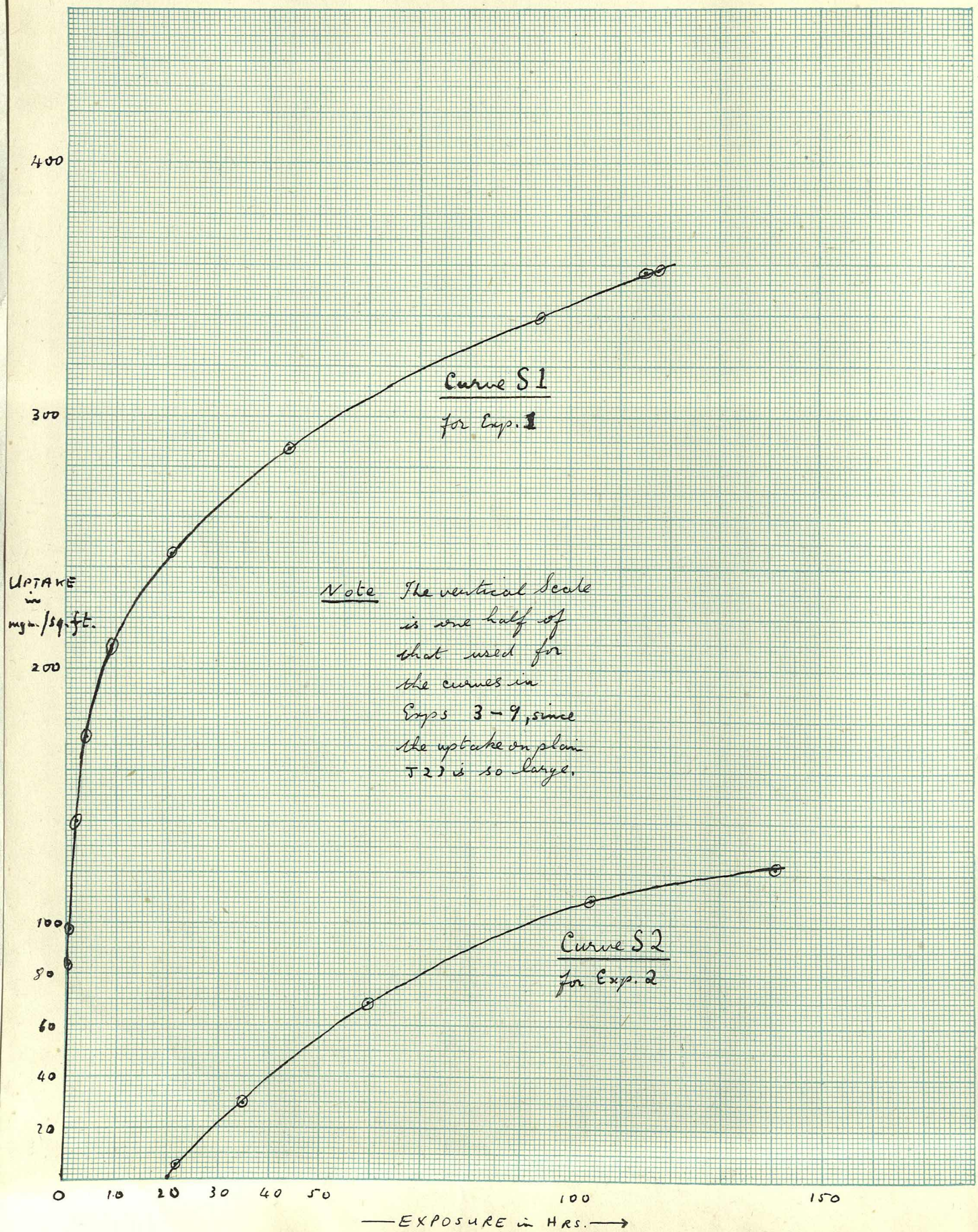
SECTION I. INTRODUCTION.

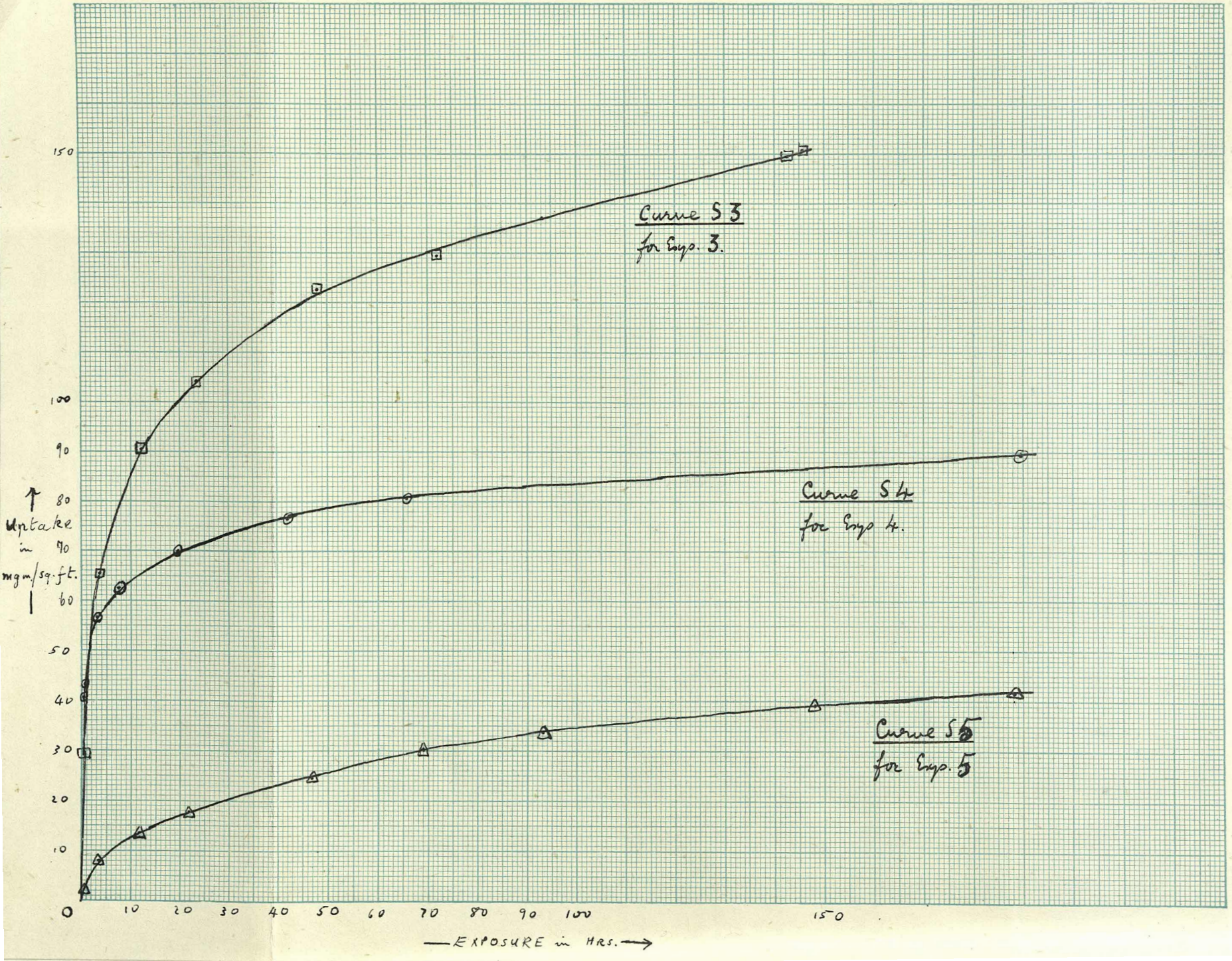
Since the main part of this thesis was presented four further curves have been obtained, two on nickel and two on aluminium. In certain of these experiments evidence was obtained that hex was liberated from the membrane (or vessel) after at least 100hrs. exposure, and experiments have been performed on oxidised nickel membrane in an attempt to repeat this, but without success.

F.T.Miles (American T.A. Report A2102) has reported a "negative uptake" when investigating the adsorption and uptake of hex on membranes stabilised by fluorine, but performed in an apparatus with a comparatively large rate of leakage (0.1mm./day or 10^{-4} mm./min.) He concludes however that the effect was due to the presence of hydrogen fluoride, which must indeed have been present in considerable quantity.

The Kohman Group (Bell Telephone Reports M976 & M930.) have reported an apparent negative uptake which they attribute to a leak. They also state that the pressure obtained by condensing the process gas with a bath of solid carbon dioxide in methanol is 2.5-10mm. "which is negligible". The vapour pressure of hydrogen fluoride at -80° C. however is of the order of 5 mm. and therefore their apparatus may have been saturated with hydrogen fluoride.

The evidence to be presented is quite inconclusive but it seems probable that a negative uptake may occur and that it may be connected with the reaction vessel rather than


400
300
200
100
80
60
40
20
UPTAKE in mgm./sq.ft.
Curve S1
for Exp. 1
Note The vertical scale is one half of that used for the curves in Exps 3–9, since the uptake on plain J23 is so large.
Curve S2
for Exp. 2
0
10
20
30
40
50
100
150
EXPOSURE in HRS.


Curve S 3
for Exp. 3.
Curve S 4
for Exp 4.
Curve S 5
for Exp. 5
Uptake in mgm/sq.ft.
150
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
150
EXPOSURE in HRS.

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the membrane.

It has also been shown that it is permissible to use oxidised nickel as a backing sheet for powder membranes as it has a very low rate of uptake after about 150hrs. exposure. It may be remarked that unlike ordinary nickel membrane in which uptake is accompanied by porosity loss, the uptake on the backing sheet alone of a powder membrane probably contributes very little to the porosity loss on exposure.

Aluminium is found to have an even lower rate of attack than nickel in both the oxidised and untreated forms.

NOTE. Membranes are referred to by reference numbers as explained in Pt. I (Note on page 43), and two new membranes are mentioned below, J108 & J112.

J108 membrane is of aluminium and was made by etching a magnesium/aluminium alloy of low magnesium content, but as shown below((Exp, 8) some magnesium remains and must have been present in the membrane used for Exp. 6, (but not for Exp. 8). It has a thickness of 2.4 mil., γ_o lies between 1×10^{-4} & 5×10^{-4}, and G is about 1.5.

J112 membrane is a coarse nickel membrane made from powder of 3.5μ diameter, using a plastic binder which was subsequently removed. It is used as a backing sheet for powder membranes.

Thickness = 7.8 mil.

γ_o lies between 15×10^{-4} & 60×10^{-4}.

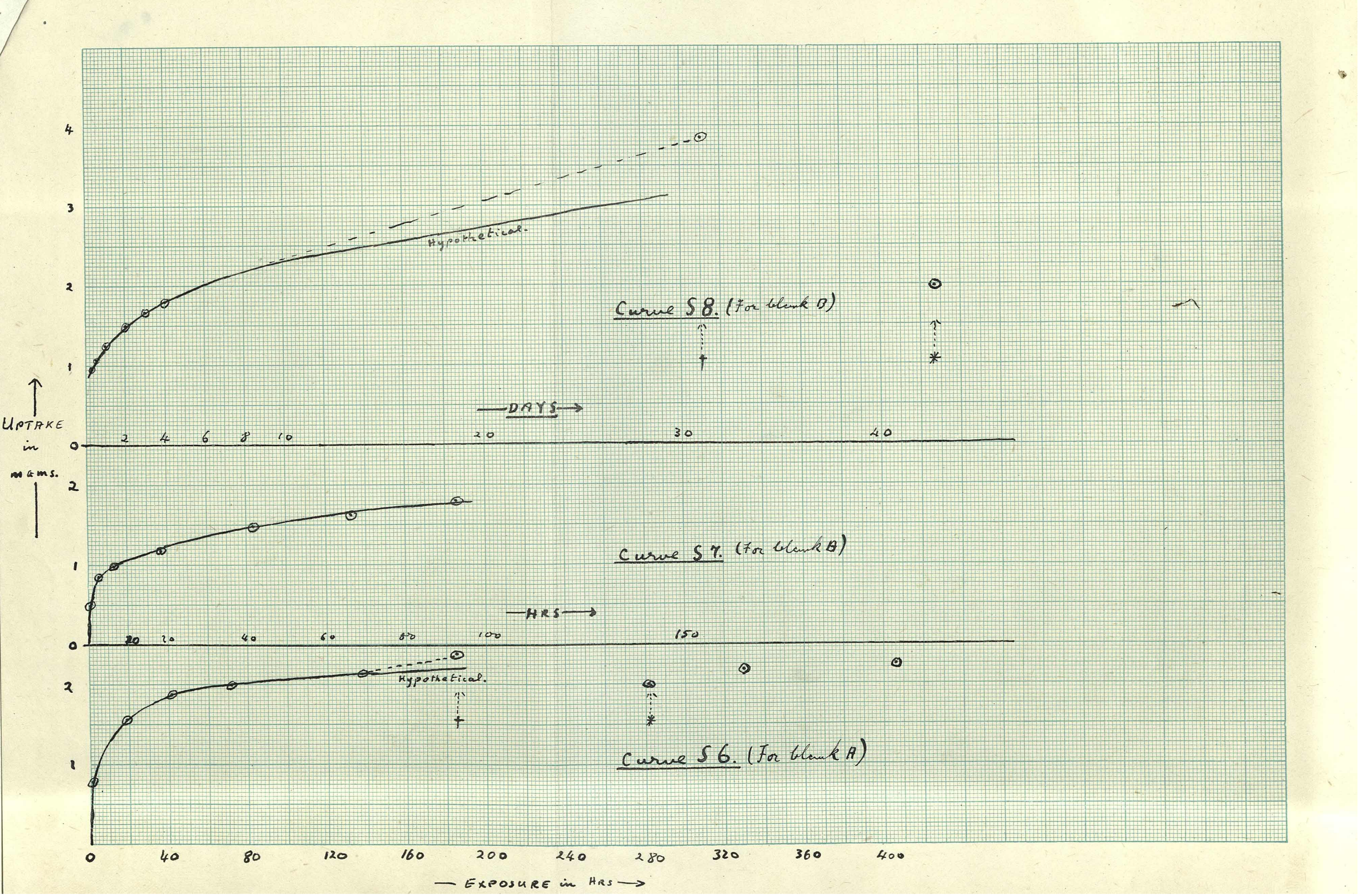
G " " 4 & 6.

Curves S1-S5 are replots of the results of Exps. 1-5 with the scale marked in mgm./sq.ft..

A document has been removed from this position and placed in Section II as enclosure number ....(1).....

Part II Supplement —

Page 2 of Section I


Curve S8. (For blank B)
Hypothetical.
—DAYS→
Curve S7. (For blank B)
—HRS→
Hypothetical.
Curve S6. (For blank A)
UPTAKE in mgms.
— EXPOSURE in HRS →

SECTION II. RESULTS.

Four experiments are to be described, for which two blank experiments were necessary. The results for these are given in Table X below.

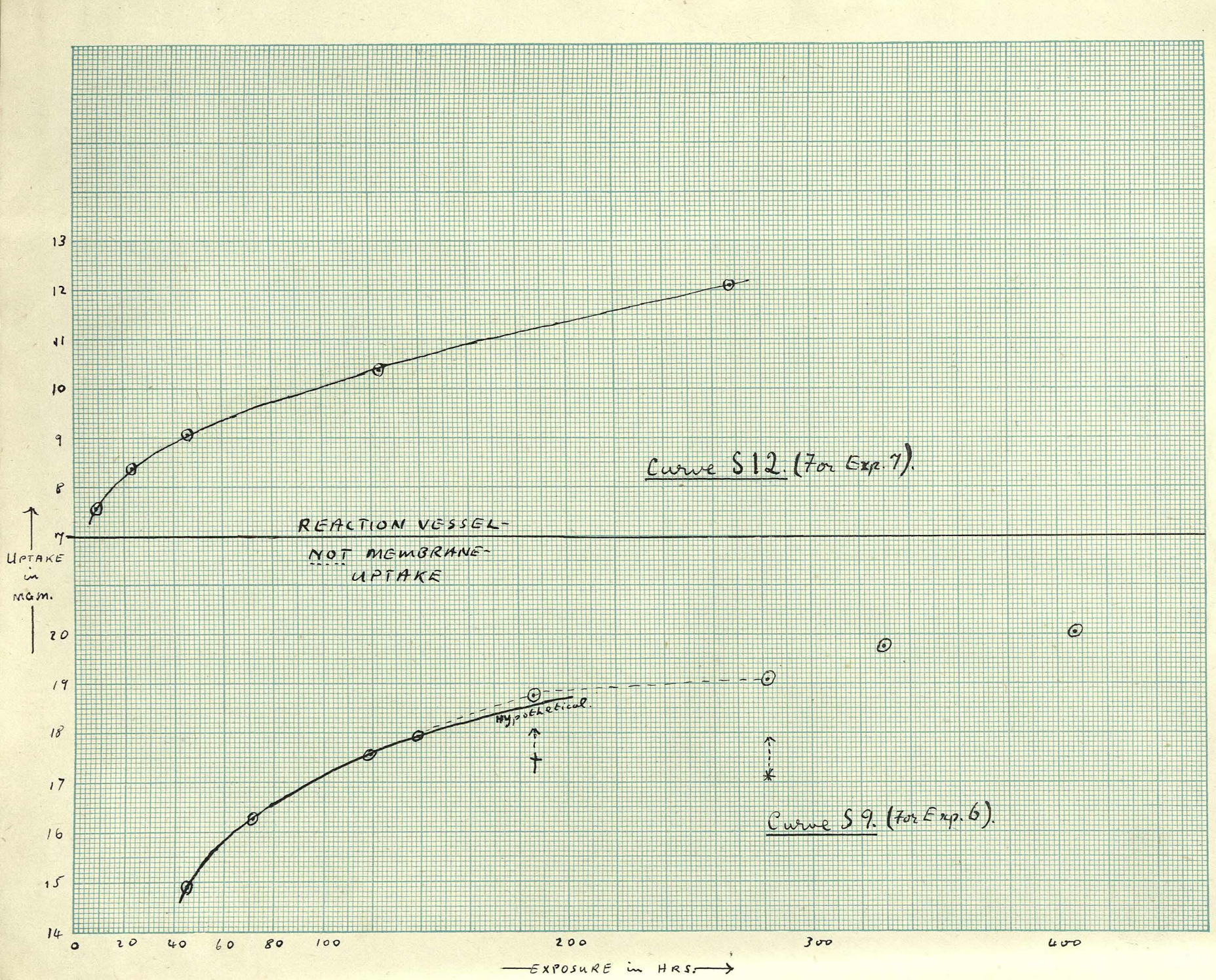
Blank A is for Exps. 6 & 7, and is plotted in curve S6, blank B for Exps, 8 & 9, and is plotted in curves S7 & S8.

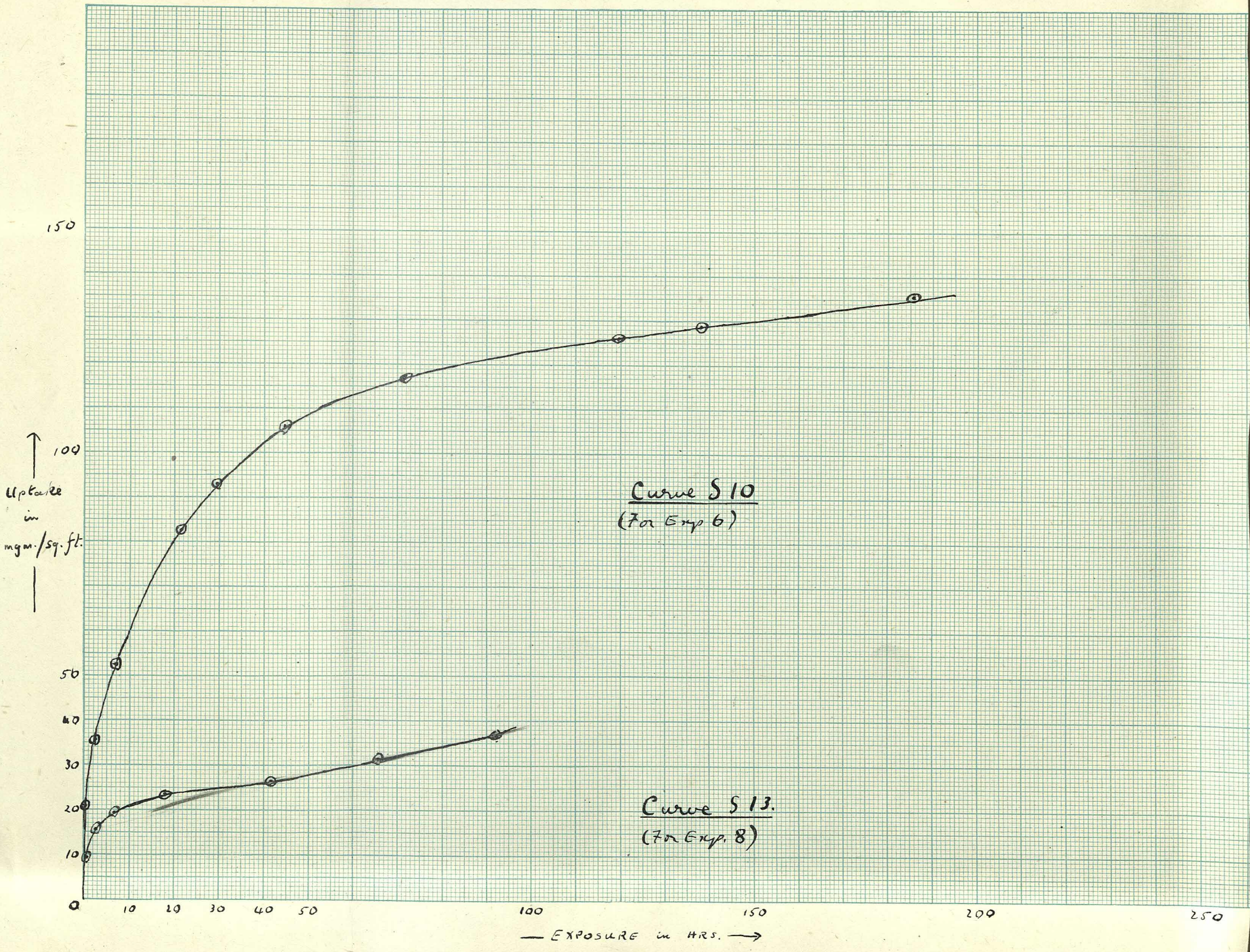
TABLE. X.

A		B		
1	2	3	4	
Total exposure. Hours.	Total uptake. mgm.	Total exposure. Hours.	Total uptake. mgm.	
¼	0.79	¼	0.49	at 1.7 mm.
18½	1.57	2½	0.85	
41	1.88	6½	0.98	
71	1.98	18½	1.17	
137	2.14	41¾	1.46	at
185	2.37†	66	1.63	33 mm.
281	2.00*	92½	1.80	
329	2.17	30dys.21hrs.	3.85†	
406½	2.24	42 " " 16 "	1.98*	

The difference between the values for A & B is due to the different previous histories of the tube, A being performed in a newly fitted tube and B inthe same tube at a later date.

/Exp.6.


13
12
11
10
9
8
7
UPTAKE in MGM.
20
19
18
17
16
15
14
0
20
40
60
80
100
200
300
400
EXPOSURE in HRS.
REACTION VESSEL-
NOT MEMBRANE-
UPTAKE
Curve S12. (for Exp. 7).
Hypothetical.
Curve S9. (for Exp. 6).


150
100
50
40
30
20
10
0
Uptake in mgm./sq.ft.
10
20
30
40
50
100
150
200
250
— EXPOSURE in HRS. →
Curve S 10
(for Exp 6)
Curve S 13.
(for Exp. 8)

Experiment 6.

To measure the uptake on 110 sq.cms. of untreated J108 membrane (aluminium) at 50° C..

Degassing: 12 hrs. at 300° C.

22 " " 200° C.

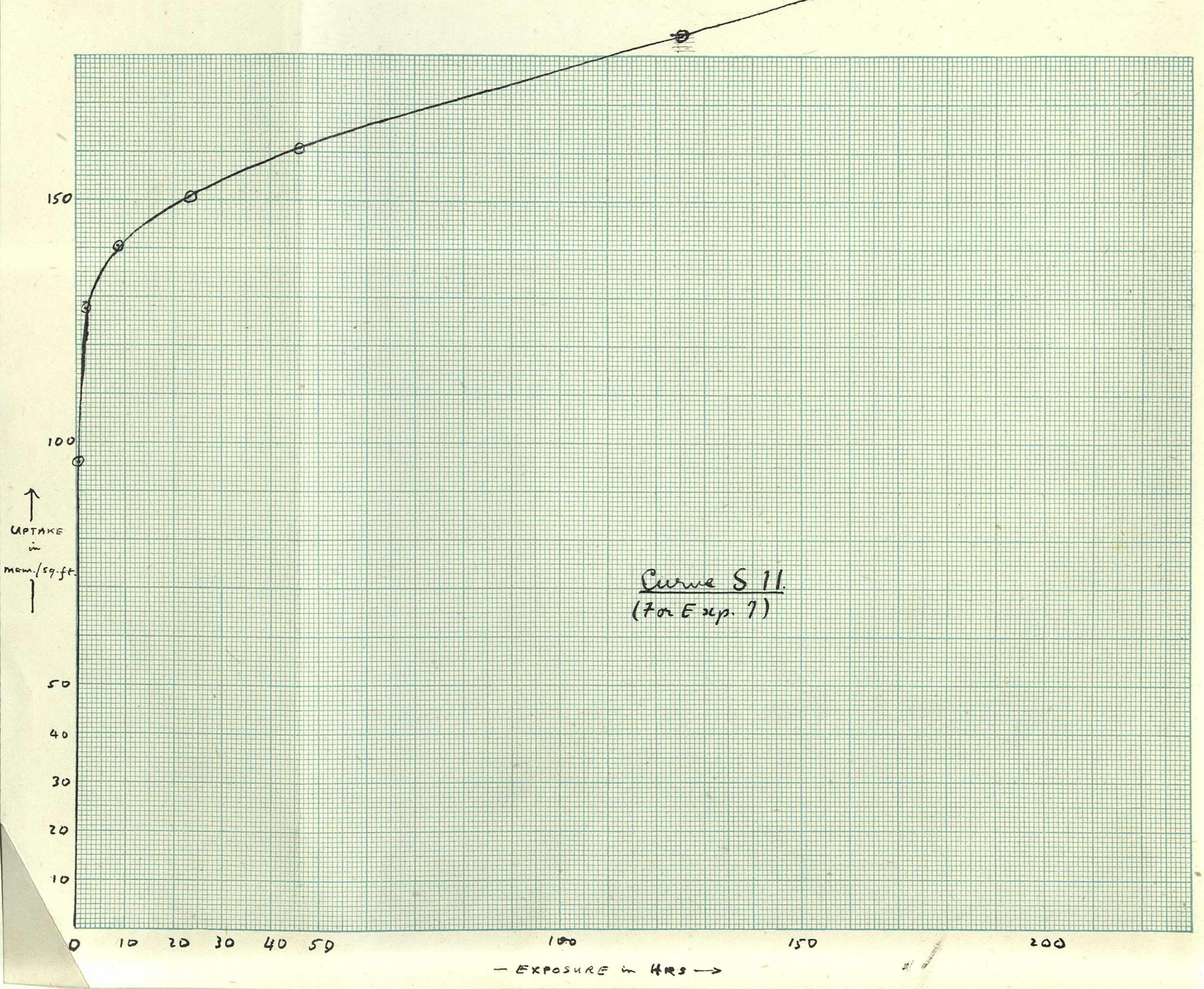
The results are given in Table XI, in which column 2 gives certain of the consumption values for the reaction vessel in mgms., and column 3 gives the uptake on the membrane alone in mgm./sq.ft.

Column 2 is plotted against time in curve S9.

" 3 " " " " " " S10.

TABLE XI.

1	2	3	
Total exposure Hours.	Total uptake in vessel. mgm.	Total uptake on membrane mgm./sq.ft.	
¼		20.55)	at 1.7 mm.
2⅓		35.5	
6½		52.2	
21½		82.8	
30		93.0	
44½	14.91	106.1	at 33 mm.
71½	16.29	116.7	
118¾	17.56	126.1	
138	17.90	128.6	
185⅓	18.72 †	134.5	
281¾	19.06 *	135.9	
329	19.72	139.8	
406¼	20.03	142.0	


150
100
50
40
30
20
10
UPTAKE in mgm./sq.ft.
0
10
20
30
40
50
100
150
200
— EXPOSURE in HRS →
Curve S 11.
(7 or E xp. 7)

The slope after 120 hrs. exposure = $3.7^{\pm 0.4}$ mgm./sq.ft./day.

Experiment 7.

To measure the uptake on 40 sq. cms. of untreated J41 membrane (nickel) at 50° C.

Degassing: 58 hrs. at 320° C.

24 " " 20° C in vacuo.

Table XII gives the results obtained and a plot is given of column 3 against column 1 in curve S11, and of " 2 " " 1 " " S12.

TABLE XII.

1	2	3	
Total exposure in hours.	Uptake in the reaction vessel. mgm.	Uptake on the membrane. mgm./sq.ft.	
$\frac{1}{4}$		95.9	at 1.7 mm.
$1\frac{3}{4}$		127.3	)
$8\frac{1}{2}$	7.56	140.3	)
$23\frac{1}{2}$	8.39	150.9	)
46	9.07	160.8	) At 33 mm.
$124\frac{1}{2}$	10.33	184.4	)
$267\frac{1}{2}$	12.10	218.1	)

The rate of uptake after 120 hrs. exposure = 6.06±0.6. mgm./sq.ft./day.

Experiment 8.

To measure the uptake on 65 sq.cms. of oxidised J108 membrane (aluminium) at 50° C.

/Oxidation.

Oxidation: (i) Degas at 20° C for 12 hrs.

" " 300° C " 56 " .

During this degassing the temperature rose to 370° C for a short time and a metallic deposit appeared on the cold parts of the tube, which on analysis proved to be magnesium. No aluminium was detected by the ordinary Group tests

(ii) Oxidise in laboratory air for 1½ hrs. at 430° C.

The porosity fell 60% as a result of this oxidation.

Degassing: 45½ hrs. at 320° C.

The results are given in Table XIII, and plotted (for the membrane alone) in curve S13.

The rate of uptake after 120 hrs. exposure < 5 mgm./sq.ft/dy.

" mean " " " during the 27dys. " = 1 ± 0.2 " "

At the end of this series of experiments a test of the kind described in paragraph iii(a) (Exp. A.) of Section III of Pt. I (p.33) was performed, with a similar result, i.e. no hex but a little hydrogen fluoride was found to be adsorbed. After standing in vacuo for 24 hrs. (but not in communication with the pumps) no renewed uptake could be neasured in half an hour.

/Table XIII.

TABLE XIII.

1	2	3	
Total exposure Hours.	Total uptake in the vessel. mgm.	Total uptake on the membrane. mgm./sq. ft.	
½		8.82	At 1.7 mm.
1½		9.03	
2¾		15.97	At 33 mm.
6¾		19.37	
18		23.47	
41½	3.35	26.31	
65¾	3.85	31.25	
92	4.70	36.87	
31 days.	8.52	63.89	
42 " 18 hrs.	7.94 *	82.62	

Experiment 9.

To measure the uptake on 104 sq. cms. of oxidised J112 membrane (nickel) at 50° C.

Oxidation: 33 hours at 340° C in atmospheric air

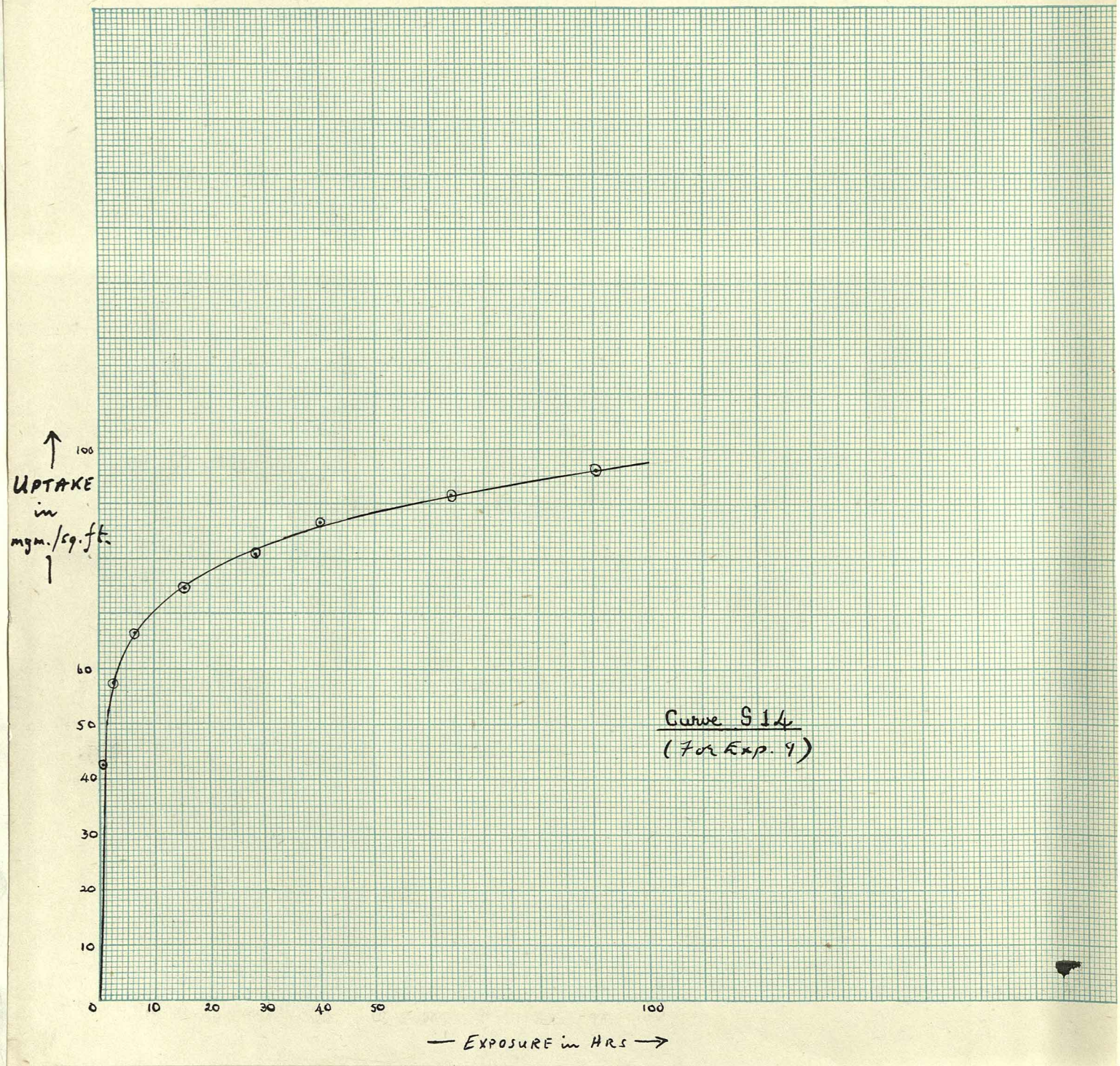
Degassing: 45½ " " 320° C.

Table XIV gives these results which are plotted in curve S14 (for the membrane alone).

The rate of uptake after 120 hrs. exposure < 3 mgm./sq.ft./dy

The mean " " " during the 27dys. " = 0.9 ± 0.2 " "

/Table XIV.



Curve S 14
(For Exp. 9)

TABLE XIV.

1	2	3	
Total exposure hours	Total uptake in the vessel mgm.	Total uptake on the membrane, mgm./ sq.ft.	
¼		42.9	At 1.7mm.
2¼		57.5	
6½		66.2	
15¾		74.64	
28¼		80.07	
40	11.43	86.38	At 3.3 mm.
64	12.25	91.66	
90½	12.90	96.01	
30dys. 20hrs.	17.75	119.8	
42 " 14 " .	17.30*	131.9	

Adesorption test was also made as in Exp. 8 with the same result.

SECTION III. DISCUSSION.

(i) "Negative Uptake.

It is possible that the apparent negative uptake shown in column 2 of Tables XB, XIII & XIV (marked in each case with an asterisk) may be due to experimental error, in the form of measuring the pressure of hex after exposure in a smaller volume than usual, (e.g. with valves 7 & 8 in Fig. 2.15 of Pt. I (facing p.23) closed). This would give a ready explanation of how, in both Exps. 8 & 9 (one on nickel and one on aluminium) and in the corresponding blank, all show a similar large effect, for the three measurements were made within one hour ofone another . But it is much less likely that the same mistake was made in measurements for blank A and Exp. 6 (curves S6 & S9), and, if it were, then the same effect should have been observedin Exp. 7. Curve S12 shows no sign of such an effect.

NOTE. Column 2 of Table XI (for Exp.6) does not show a negative uptake, but the plot of these readings (curve S9) shows a definite break as if a negative uptake had occured, but was masked by a slightly larger positive uptake. This can be explained by assuming an uptake on the membrane and a negative uptake on the vessel, and whichever is the greater determines the sign of the resultant observed uptake (see below).

It is noteworthy that in Exp. 6 and those on the two blank tubes the uptake in the period of exposure immediately preceding that in which a negative uptake was observed,(or deduced in the case of Exp. 6) was abnormally large (figures

marked with a dagger in column 2 of Tables XA, XB & XI, and broken lines in curves S6, S8 & S9). The same effect if present in Exps. 8 & 9 is masked on the graphs on account of the long exposure (27 days). At the same time also a relatively large amount of hydrogen fluoride was formed. It is also apparent that the effect, if real, is greater in the blank than in the reaction vessel, and when the results for the blank are subtracted from those for the reaction vessel the negative uptake is more than compensated for, which suggests that the phenomenon is concerned with the vessel rather than the membrane.

With these points in view an attempt was made with two samples of oxidised and pretreated nickel (J41) membrane to repeat the negative uptake, but with no success.

(i) The membrane was stabilised by exposure at 120° C for 8 hrs. and at 50° C for 84 hrs.

(ii) A large uptake was brought about by exposure at 150° C for 24 hrs.
This was accompanied by the formation of a large quantity of hydrogen fluoride.

(iii) The membrane was allowed to stand for 24 hrs in vacuo at 25° C.
No hex appeared in the tube.

(iv) An exposure of 28 hrs. at 125° C. was then made in the presence of 3-4% of hydrogen fluoride.
The uptake was smaller than expected but the result was not conclusive.

(v) A month's exposure at 50° C resulted in a normal

/uptake

uptake and little hydrogen fluoride was formed.

(vi) In the next 12 days at 50° C there was no negative uptake. (Compare with Exps. 8 & 9 in which a month's exposure resulted in the formation of much hydrogen fluoride, and a negative uptake followed in the next period).

(vii) The hex pressure at the beginning of the next 12 day exposure at 50° C was reduced to 20% (ca.6mm) of the usual figure.

No hex was liberated.

The matter therefore remains in the balance, but the probability is that the effect exists and it may be concerned with the reaction vessel. It may also be in some way connected with the liberation or formation of large amounts of hydrogen fluoride in the reaction vessel.

The effect was not found in any of the experiments 1-5 and this may be due to the fact that the tubes in which Exps. 1-5 were performed were thoroughly treated with hex at 90° C before use. Exps. 6-9 were performed in new tubes or tubes only slightly attacked.

A possible reason for its concerning the vessel and not the membrane is that when liquid air is applied to the tube for a few seconds the tube is probably cooled more than the membrane, whose contact with the tube is poor.

In any case nothing can be said at this stage, but there is no reason to doubt the validity of results obtained by

/this

method if the experimental points lie on a smooth curve, i.e. the results of Exps. 1-5, and of Exps. 6-9 for the first 100 hours may be relied upon.

(ii) General.

The table on p.55 of Pt. I is brought up to date below

Exp. No.	Type of membrane	Uptake in mgm./sq.ft. after 12	60	120 hrs.	Rate of uptake after 120 hrs. Mgm./sq.ft./dy.
1	Untreated J23.	218	307	359	17.7 ± 0.8
2	" " .	-	-	-	14.0 ± 0.7
3	Oxidised " .	90	126	147	6.6 ± 0.7
4	" " & very well degassed.	66	80.4	86	1.9 ± 0.2
5	Oxidised J41 & pretreated.	13.7	27.8	37.1	2.4 ± 0.3
6	Untreated J108(Al)	65.7	113	126.5	3.7 ± 0.4
7v	" J41	143.3	165.6	183.5	6.0 ± 0.6
8	Oxidised J108(Al)	20.2	30	-	< 5) Mean slope
9	" J112	72	91	-	< 3) in next 27 days = 1 mgm./sq. ft./day

Experiments 5 & 7 confirm that oxidation of nickel reduces the attack by at least 50%, which was observed for Exps. 1 & 3. It is likely that much hex was taken up in Exps 5 during the pretreatment and therefore the oxidised J 41 membrane is not so much better than the untreated J41 as may appear from the figures above. In both sets of experiments the slope after 120 hours is about 3x as large for unoxidised

/as

as for oxidised membrane,

Oxidised J108 (aluminium) appears to have an uptake of about 1/3 of that of plain aluminium (Exps. 6 & 8), but these results are rendered doubtful by the poor quality of curve S13 for oxidised aluminium.

SECTION IV SUMMARY

The evidence so far obtained points to the existence of an effect, called for convenience a "negative uptake", which is characterised by the appearence of more hex in the reaction vessel at the end of an exposure than was put in at the beginning. This seems to concern the vessel rather than the membrane, and is influenced by the presence of hydrogen fluoride. The possibility of experimental error must be borne in mind, especially as two other investigators have found the same effect to be due to errors of technique (Introduction to the Supplement p. 1). It is hoped that thorough stabilisation of the tubes before use will eliminate the effect.

It has been shown that oxidised nickel membranes can be obtained of suitable stability for the preparation of powder membranes for plamt work; and it is probable that oxidised aluminium has greater stability than oxidised nickel, from the point of view of uptake.