"Techniques for the Assay of Tritiated Compounds and the Measurement of small Vapour Pressures."

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Abstract

Several different methods for the gas phase assay of tritium have been investigated and a simple and rapid assay technique has been developed.

This method has been used to measure the partial pressure of water in aqueous dioxan solutions at 18°C and at 25°C, in a concentration range where the partial pressures are too low to be readily measured by other methods.

Partial excess thermodynamic functions of mixing have been calculated from the pressure measurements.

Acknowledgement

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CONTENTS

SECTION A TRITIUM ASSAY

SECTION B VAPOUR PRESSURE MEASUREMENTS

SECTION B II.

SECTION C THERMODYNAMIC PROPERTIES OF AQUEOUS DIOXAN

A. TRITIUM

I. Introduction

Tritium is a radioactive isotope of hydrogen which occurs naturally as the result of the reaction between cosmic ray neutrons and nitrogen in the upper layers of the atmosphere.

$$N^{14}_{7} + n^{1}_{o} = C^{12}_{6} + H^{3}_{1}$$

Neutron capture by nitrogen may also result in the formation of carbon - 14

$$N^{14}_{7} + n^{1}_{o} = C^{14}_{6} + H^{1}_{1}$$

and this reaction has been shown experimentally by Libby & Cornog[1] to be about 100 times more probable than the first.

Because of this, and also because of its much shorter life, tritium is much less abundant in nature than carbon-14, the relative proportions being of the order of $1:10^{6}$. The proportion of tritium in rain water has been found to be approximately 1 part per trillion, but none is detectable in glacial water[2].

Tritium can also be produced artificially, for example by the bombardment of lithium with neutrons.

$$Li^{6}_{3} + n^{1}_{o} = He^{4}_{2} + H^{3}_{1}$$

The gas obtained emits beta particles of very low energy (Max.0.015 Mev) has a half life of 12.26 years and the very high specific activity of 2.7 curies/standard ml.[12b] This decay rate is very convenient for tracer work. It is slow enough to remain practically constant throughout most experiments yet fast enough to permit very high count rates. Tritium is cheap, and, because of the low energy of its radiation, relatively safe.

In spite of these advantages and its potential usefulness tritium has not been very extensively used, possibly because of the assay difficulties. The beta particles emitted are too weak to penetrate the window of an end-window counting tube and can only be detected if the emitter itself is within the sensitive volume of the detector. It is therefore essential to introduce the tritiated material into the body of a counting tube, a procedure which requires the use of a vacuum line, more or less complicated, according to the nature of the filling mixture. More recently, scintillation counting[3,4,5], which is quicker and simpler but less efficient, has gained favour. Unfortunately hydroxylic substances cannot at present be satisfactorily assayed by this method because of their immiscibility with the liquid scintillator and their absorption of light.

Water of very low tritium content has been assayed visually in a cloud chamber by Fireman[2] who was interested in the proportion of tritium in natural water.

A second difficulty encountered in handling tritiated compounds arises from the ease of exchange between hydrogen and tritium atoms. Exchange is immeasurably fast between hydrogen atoms linked to oxygen or nitrogen, and very slow between hydrogen linked to carbon unless the latter is activated by for example an adjacent keto group. This subject has been reviewed by Kimball[6] and Satchell & Gold[7]. Surprisingly fast exchange is reported between tritium gas and aromatic compounds, even when the latter contain no activating groups. Thus, Wilzbach[8] mixed 7.5C tritium gas and various aromatic compounds and found that after 3 days 0.86 gms. of e.g. Toluene, had acquired an activity of 42.7 mC. It follows that the results of experiments involving tritium may be seriously misinterpreted unless every precaution is taken to exclude or allow for exchange reactions. Contamination of glassware and exchange with atmospheric water vapour are potential sources of error particularly if small quantities of material containing hydroxylic tritium have to be manipulated.

GAS COUNTING OF TRITIUM

The great variety of published methods of tritium assay suggest that none of them is completely satisfactory. Although the electronic equipment used by different workers is far from standard, the main difference between these different techniques is in the form in which the tritiated material is introduced into the detecting device. The performance of the latter, which may be an ionization chamber or a Geiger Muller counting tube, is dependent on, among other things, the nature of the filling gases. A Geiger filling for example is not suitable for assay purposes unless the count rate remains almost constant when the voltage applied across the electrodes is varied. The relationship between the count rate and voltage is the "characteristic" of the tube, a "good" characteristic having the form shown below.

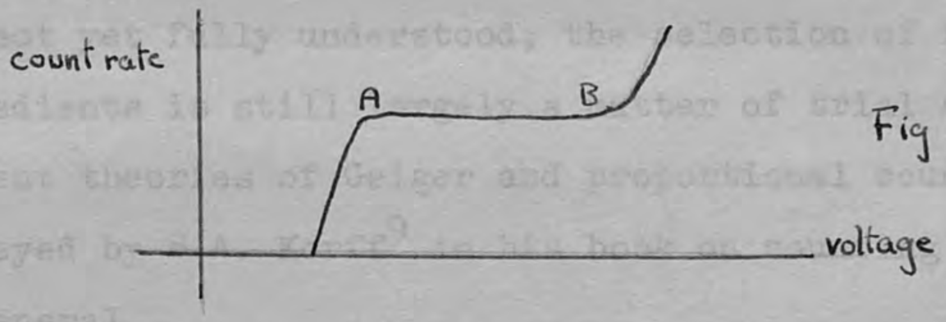


Fig (1)

If a tube is operated at a voltage greater than A it is said to be functioning in the "Geiger region". This is a voltage range within which all the discharge pulses are of the same size irrespective of the size of the ionizing event which initiated them.

Below this voltage the pulse sizes are roughly, and in certain conditions, exactly proportional to the size of the initial ionizing event. A tube is operated in the "proportional region" if it is necessary to distinguish between pulses arising from different types of radiation, for example if a low activity source has to be counted against a high background count.

A filling is generally considered satisfactory for assay purposes if it gives a plateau at least 100 volts long with a slope of not more than 3% per 100 volts. Some gases which do not give a Geiger plateau can be counted at a lower voltage in the proportional region if a pulse size discriminator is available, but as this requires more expensive equipment it seems more advantageous to choose a gas which does have a Geiger plateau.

As the processes which occur within the counting tube are not yet fully understood, the selection of filling ingredients is still largely a matter of trial and error. Current theories of Geiger and proportional counting are surveyed by S.A. Korff[9] in his book on counting techniques in general.

The noble gases and saturated hydrocarbons have proved to be good fillings and form the basis of most of the mixtures used for tritium analysis. Oxygen, nitrogen and halogens are undesirable in a counter because of their tendency to form negative ions[10] sufficiently mobile to cause spurious pulses[11]. These may cause the total disappearance of the plateau, or a marked increase in its slope.

Water vapour has approximately the same electron attachment coefficient as oxygen and for this reason was until recently usually excluded from counter fillings.[9a,12a,13]

The poor counting properties of water vapour are particularly unfortunate because in many physico chemical problems e.g. in the present work, the measurement of small quantities of water are fundamental. In biochemical tracer work, labelled organic compounds are usually oxidised to carbon dioxide and water, so that here too, direct counting of tritiated water would be useful.

A few workers have attempted direct water counting. Fontana[14] used a filling containing 1cm Hg pressure of water vapour and 2 cms propane. He gives no details of the Geiger characteristic. Another group[15] claims that provided the pressure of water vapour is kept below 2 mm counter characteristics are not adversely affected. The filling was made up with 2.5 cms of absolute ethyl alcohol and 2.0cms of argon. In order to compensate for the very small volume of tritium which could be introduced into the counter at this low pressure they used a specially constructed counter with a volume of 1 litre. Full details of the Geiger characteristic of this rather unusual filling are not given. The mean standard error was ± 3.7%.

In 1955, Cameron[15] stated that a tube containing 1 cm of ethyl alcohol and 10 cms argon (a standard filling with excellent counting properties) would tolerate a pressure of 1.5 cms of water vapour without any deterioration of the characteristic. He was not interested in tritium assay and so did not recommend the filling for this purpose. So far (1959) no one has adapted this filling to the estimation of tritium.

A filling consisting of helium saturated with water has been described by Bradley and Bush[17] who were seeking a simple means of tritium assay suitable for routine work in hospitals.

Several general papers on aqueous fillings[18,19] suggest that even if an aqueous filling with a satisfactory Geiger characteristic were found, it would probably be unsuitable for tritium assay because of the absorption of water vapour by glass (Drever) or exchange with deep seated molecules in the glass of the counter (Grenon). Experiments with polythene counters are proposed by Drever as a solution of these problems.

Counter tubes are always heavily contaminated by tritiated water fillings, the count rate after prolonged pumping out may be as high as 20% of the initial count. This was held to be a serious disadvantage and led to drastic and lengthy decontamination procedures (e.g. Pace et al[15]) until Cameron showed that the background could be reduced to normal by simply flushing several times with inactive water vapour.

Indirect methods of estimating tritiated water fall into two classes:- (a) those which incorporate the tritium in another molecule by exchange, and (b) those which convert the water chemically into another molecule.

To class (a) belongs one of the earliest and simplest methods of tritium assay. This was developed by Black, Joris & Taylor[20] who were using tritiated water for the measurement of the solubility of water in aromatic hydrocarbons. After equilibrating the two liquids, the combined vapours were passed through a column of calcium oxide in order to convert all the water to calcium hydroxide. The organic vapours were pumped off and the drying agent, now containing partially tritiated hydroxyl groups exposed to the vapour of absolute ethyl alcohol. The tritiated alcohol thus obtained was introduced into a counting tube and the filling was made up with argon to give the standard 10:1 argon alcohol mixture.

This filling has been used for many purposes and has been fully investigated by W.D.P. Spatz[21] who found that in the right conditions plateaus at least 400 volts long and having slopes less than 1% were readily obtained. This filling was used in the early part of the present investigation and gave even better results, plateaus 1000 volts long with slopes less than 0.5% being not uncommon. Although the characteristics of this filling could scarcely be bettered the method as a whole is not ideal for tritium estimation. The ratio of argon to alcohol is critical, plateau slope increasing rapidly with increasing proportion of alcohol (Spatz ibid). The amount of tritiated vapour which can be assayed is therefore limited because the optimum total pressure in the counter is ca 15cms. Accurate measurement of about 1.50cms pressure of alcohol vapour is difficult, on an ordinary manometer an error of about 3% would be expected.

A more recent technique of this type depends on the base catalysed exchange of tritiated water with acetone, (Bradley and Bush ibid). Their filling consisted of helium saturated with the vapour of tritiated acetone and gave a plateau of slope 5% at 2500 volts. The use of acetone instead of for example alcohol has the advantage that all six of the acetone hydrogens exchange so that at the same pressure of vapour in the counter a count rate six times as high can be obtained. It has on the other hand the disadvantage of a longer exchange time, but as this exchange is very slow unless catalysed there is the compensating advantage that the active acetone will not contaminate the tube, nor will it lose activity during handling.

Recently a method of tritium assay has been described which bears some resemblance to that finally developed during this research. In this new method the tritium containing substance to be assayed is allowed to exchange with ammonia and the latter admitted into a G.M. tube. The counting properties of ammonia are apparently poor because it was found necessary to introduce methane in order to obtain a workable characteristic. Using a mixture of 80.35cms pressure methane and 4.5cms pressure of ammonia, a 200 volt plateau with a 0.5% slope occurs at a voltage of 4200.

The more important techniques of class (b) were reviewed by Glascock[12b] in 1955. Most of these depend either on the reduction of water to hydrogen with Zn dust, magnesium amalgam or lithium aluminium hydride or on the conversion of water to a hydrocarbon by reaction with a carbide or a Grignard reagent.

Hydrogen has poor counting properties and some workers prefer to use an ionization chamber as detector.[22,23] Alternatively a Geiger tube can be used in conjunction with a proportional counter.[24]

Geiger counting with various mixtures of hydrogen, ethanol, helium and argon is described by M.D. Kamen[25] but as the only characteristic mentioned is a plateau length of 40 volts these methods do not seem to be promising.

A more recent paper[26] gives details of a quench circuit the use of which permits Geiger counting of pure hydrogen gas at atmospheric pressure. The plateau begins at 3100 volts, which is remarkably low for such a high pressure filling, and has a slope of 1%. This would appear to be the most satisfactory method of hydrogen counting.

Acetylene,[28] methane[29,30] and butane[12c] have been used as counter fillings. The methane fillings showed no Geiger region, a fact which is attributed to impurities such as H_2O, H_2S and NH_3 arising from the reactants (D.F. White). Methane has therefore to be counted in the proportional region, a procedure which is much more expensive and complicated than Geiger counting, where fairly good characteristics can be obtained (200 volts, 3%).

Butane is much more easily handled than either hydrogen or methane because it is completely condensed at the temperature of liquid air and can therefore be quantitively and easily transferred from one part of the vacuum line to another. This method of tritium gas counting seems to be the only one to have found favour among workers independent of its inventor.

The Geiger characteristics are good (800 volts, 3%) but at the optimum pressure of 14cms the starting voltage is 3200 volts which is rather high for convenience. At this voltage electrical leakage across the terminals of the Geiger tube may cause spuriously low count rates or occasionally, a complete cessation of counting. To prevent this Glascock recommends that the glass surrounding the electrodes be treated with a silicone polymer.

Unfortunately in order to obtain good counting characteristics and consistent results a lengthy and rather exacting procedure must be followed in preparing the butane.

$$H_2O + C_4H_9MgBr = C_4H_{10} + Mg\ OH\ Br$$

An ethereal solution of butyl magnesium bromide is prepared from rigorously dried and purified reagents. Portions of this solution are then transferred to reaction tubes, attached to the vacuum line and the ether pumped off. It is then necessary to bake the reagent under high vacua for two hours at a temperature not greater than 120 C and not less than 110 C. Too high a temperature damages the reagent, too low a temperature results in unreliable analyses due to the formation of inactive butene in the subsequent reaction of water. Fresh supplies of reagent must be prepared every week because "ageing" is also conducive to butene formation.

The final process, the reaction with water, is conducted by heating for one hour at 120 C, the butane so formed being measured manometrically and then condensed into a Geiger tube.

Results obtained by Glascock were reproducible to within ± 2%. As the tritium introduced into the tube is directly attached to carbon, contamination in the usual sense does not occur, but the solubility of butane in the vacuum grease was occasionally a source of error.

A.

II. Preliminary Work on Tritium Assay

(i) SELECTION OF ASSAY TECHNIQUE FOR THE PRESENT WORK

The factors governing our choice of method were:-

(a) the reliability of apparatus commercially available

(b) the adaptability of the method to measurement of microgram quantities of tritiated water in the presence of excess dioxan

(c) reliability

(d) the speed and simplicity of assay.

The electronic equipment which had been chosen was a Dynatron 4Kv power pack, an Ericcson Decatron scaler, a probe unit and a number of 20th century GA/IOM gas counting tubes.

Those techniques requiring proportional counters or ionization chambers had therefore to be excluded.

Considerations (b) and (d) suggest that one of the direct methods would be the most logical choice. The reliability of these is however questionable.

The reliability of tritium counting techniques in general is difficult to assess because many of the publications give inadequate details of characteristics and reproducibility.

Butane counting, as developed by Glascock, appeared to be the most satisfactory in this respect, but unfortunately the assay procedure is long and relatively complex. As Glascock himself estimated that in an average week a full time assistant would be unable to assay more than 18 samples it was apparent that for a single handed worker the time involved would be prohibitive.

It was therefore decided that the reliability of the methods of Cameron and Joris et al should be investigated and that the adaption of the method of Bigg's for use with a Geiger counter should be attempted.

(ii) THE VACUUM LINE

The degree of vacuum required for gas counting of radioactive isotopes is a matter of dispute. While the majority of workers in this field recommend the use of diffusion pumps, Cameron[16] found that a mechanical pump giving a vacuum of 10^{-3} mmms was adequate. Anderson,[31] et al, claimed that a diffusion pump was not only unnecessary but undesirable. They obtained erratic results when using high vacua and attributed this irreproducibility to desorption of gases from the glass walls of the system.

The use of oil rather than mercury pumps is sometimes recommended on the ground that the latter has a deleterious effect on counting properties.[29] This subject was investigated by Korff and Present,[32] who concluded that at room temperature the small amount of mercury present in the geiger tube had no harmful effect. Abnormal results were however observed at higher temperatures.

The pumping system chosen for this work comprised a two stage rotary pump backing a mercury diffusion pump, but after a few month's experience it became clear that the latter was not essential.

Much later in this investigation a geiger tube was filled using no other source of vacuum than an ordinary water pump. The characteristic obtained was remarkably good, Fig. (18). This very surprising observation is of great interest because the rigorous exclusion of both water and oxygen is a recurring theme in the literature of this subject. It is unfortunate that this experiment was not attempted earlier as it would have saved many time consuming and quite unnecessary precautions, such as for example, the thorough degassing of all liquid samples, the removal of oxygen from the argon and the search for suspected, but non-existent, leaks.

The operative parts of the original vacuum line are shown in Fig. (2).

The counting tube is attached to the system at the B.10 joint J_{gm}. S_1 and S_2 are sample tubes fitted with B.10 sockets and containing tritiated water, alcohol etcetera; S_3 is a similar tube containing inactive water for decontaminating the line.

That part of the system bounded by the taps $T_4 T_5 T_6 T_7$ and T_8, hereinafter referred to as the manometric chamber,

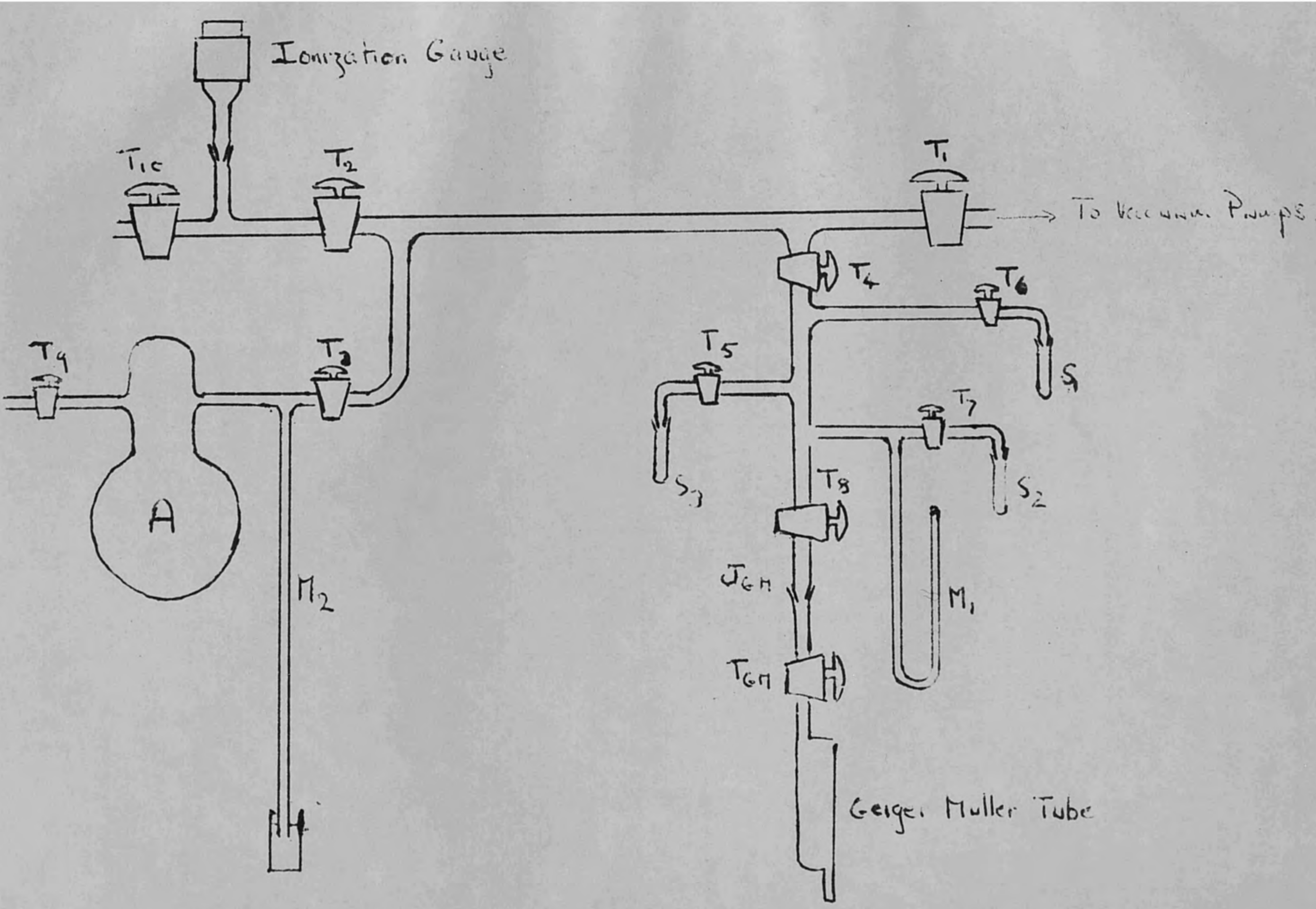

Ionization Gauge
T10
T2
T1
To Vacuum Pumps.
T4
T6
S1
T9
T3
T5
T7
S3
S2
T8
A
JGM
M1
M2
TGM
Geiger Muller Tube

Fig (2)

had a known volume of approximately 75 mls. This volume was determined by attaching a flask of known volume, containing various pressures of argon to the joint J_{gm} and measuring the final pressure after allowing the argon to equilibrate with the previously evacuated chamber. The volume thus measured includes the space bounded by the tap T_8 and the tap on the calibrated flask. In order to obtain the true volume of the manometric chamber, this small volume had to be measured and substracted from the total. This was most conveniently done by closing T_8 and the tap on the flask after each equilibration pumping the surplus gas away, closing T_4 and allowing the small amount of gas trapped between T_8 and the tap on the calibrating vessel to equilibrate with the manometric chamber. From the ratios of the pressure before and after this operation and the total volume determined in the first equilibration the small volume can be calculated.

M_1 was a U tube mercury manometer prepared and filled in the manner described by Glascock.[12d]

The manometer M_2 was simply a straight tube dipping into a small flask of mercury.

The two litre bulb A contained argon ar a 10:1 mixture of argon and alcohol, depending on which assay method was in use.

(iii) PROCEDURE FOR FILLING COUNTING TUBES

The sample to be analysed was transferred to a sample tube and attached to one of the joints behind T_6 or T_7. It was then degassed by freezing in liquid air and evacuating to 10^{-4} mm Hg and then allowed to warm up with the tap above it being closed. This was repeated twice more . The counting tube was then attached at J_{gm} and pumped out to 10^{-3} mm for a few minutes, all taps except T_1 T_4 T_8 and T_{gm} being closed. T_4 and T_8 were then closed and the appropriate pressure of tritiated vapour (calculated from the respective volume of the tube and the manometric space) admitted to the chamber by cautiously opening T_6. Cautiously, because it was preferable to reach the desired pressure in a gradual and not in an oscillatory manner.

The known weight of active vapour was condensed into the counter tube by closing T_6 opening T_8 and T_{gm} and immersing the trap at the bottom of the tube in liquid air.

In order to introduce the argon or argon:alcohol mixture T_4 was opened T_1 closed and T_3 opened until a pressure of about 20 cms was registered. After closing T_3, T_{gm} was opened gradually so that the pressure fell smoothly to about 10 cms. T_{gm} was then closed and after allowing 15 minutes for the gases to diffuse the tube was connected to the counting equipment and the count rate determined.

(iv) DECONTAMINATION

The errors which arise from the "memory" of a tube which had formerly contained tritium is well known, but the equally serious problem of contamination of the vacuum system seems to have received very little attention.

As contamination is not completely removed even by pumping for several hours in high vacuum, the only convenient procedure for eliminating this source of error is to flush the system several times with inactive water vapour as recommended by Cameron.

This was accomplished by attaching the contaminated tube to J_{gm} Fig. (2) evacuating the relevant parts of the system, closing T_4 and opening T_5. It was usually sufficient to expose the line five times to fresh water vapour.

Decontamination by this method can give rise to spuriously low count rates, because of the exchange between inactive water remaining on the walls of the manometric chamber and the next sample of active vapour to be analysed.

A rough calculation, based on the work of Bent and Leswick[33], shows that an error of about 2% could arise in this way. This source of error was eliminated by flushing the manometric chamber, but not the geiger tube, with the vapour from the sample to be analysed. The surplus vapour was then pumped away into a liquid air trap.

(v) THE GEIGER TUBES

These were of conventional design, the anode being a tungsten wire approximately .005 cms in diameter coaxial with a stainless steel cylindrical cathode. The capacity of the tubes was about 110 mls and the background count when shielded in a lead castle was about 60 counts per minute.

Initial attempts to obtain a geiger plateau, using the 10:1 argon alcohol mixture were completely unsuccessful, the tubes going into continuous discharge as soon as the threshold voltage was reached. Considerable delay resulted from our failure to suspect the tubes, the poor characteristics being attributed to the newly constructed vacuum line and inexperienced manipulation. Apart from leaks the main suspected sources of error were traces of oxygen in the argon and in the alcohol. No improvement was observed when the argon was purified by passage through a charcoal trap cooled in liquid air, nor with repeated degassings of alcohol.

Finally the tubes were tested at Harwell by Cameron and found to be faulty.

Subsequent experience suggested that a tube which was initially "faulty" could be induced to work by persistent evacuations and fillings with argon. Prolonged pumping at 10^{-5} mms was not of itself sufficient. Flaming under high vacuum was also ineffective.

This problem which is widely observed is sometimes attributed to oxygen occluded in the central wire. For this reason some workers prefer to construct their own tubes, in which the anode has an external connection at the top and bottom of the glass envelope, so that it can be flashed by the passage of an electric current.

A second difficulty sometimes encountered, which is possibly related to the first problem, was the resistance of some new tubes to decontamination. One pair of tubes gave poor but workable plateaus on arrival, but after having been used once for tritium assay, the background could not be reduced to normal by the usual procedure of flushing with water vapour. Decontamination was eventually effected by pouring about 2 mls of water into the tube and boiling it. Tubes which had been treated in this way suffered no observable ill effects and were still functioning satisfactorily after 18 months.

A possible explanation of this effect would be the presence of occluded hydrogen in the tungsten, in which case the best cure for the trouble would be to "flash" the central wire.

A third very troublesome property of some tubes of this type was their very high photosensitivity. Tubes bought in the early stages of this investigation were moderately sensitive to light; if exposed to direct sunlight the count rate increased by a factor of two or three. Tubes bought at a much later date were much less satisfactory, the background count increasing nearly a thousandfold in sunlight.

Although this problem can be solved superficially by excluding light during counting, energetic radiation is emitted within the tube as a result of the discharge processes and it is not possible to ensure complete protection against this. It was considered that spuriously high counts might be obtained with these tubes and they had therefore to be rejected.

(vi) COUNTER CORRECTION

As the counting efficiency varies slightly for different tubes, one tube was chosen as a standard and the relative efficiency of the others expressed as a percentage.

The serial number of the tube was always recorded when a count rate was determined so that the correction for efficiency could be applied.

(vii) DEAD TIME CORRECTION

The dead time of the counting equipment was controlled by a selector switch in the probe unit. In normal geiger fillings the discharge mechanism itself results in a dead time of between 150 - 250 micro seconds. The selector switch was therefore set at 300 micro seconds, the observed count rates being corrected for this dead time loss before deduction of background count and correction for the efficiency of the tubes.

(viii) TRITIATED WATER

The initial sample of tritiated water had a volume of 0.2 mls and an activity of 1 Curie. The phial containing the sample was opened in a fume cupboard, rubber gloves being worn at the time.

Four weaker tritiated solutions having the specific activities shown below were prepared.

Solution	Activity/ml	Diluent
I	40 mC	water
II	4 mC	water
III	60 µC	ethyl alcohol
IV	60 µC	water

Table (1)

(ix) INVESTIGATION OF CAMERON'S METHOD

The vacuum line is shown in Fig. (2). The bulb A contains a 10:1 mixture of argon and alcohol and the tube S, a sample of tritiated water.

Mixtures of 1.0 cm pressure of water vapour and about 10 cms of the argon alcohol mixture were admitted to the counter tube using the filling procedure described earlier.

Despite repeated attempts, characteristics resembling those of Cameron were never obtained. The argon:alcohol mixture alone gave a good characteristic but this was ruined if water vapour was admitted.

Argon - Ethyl Alcohol Filling

Effect of Water on Geiger Characteristic

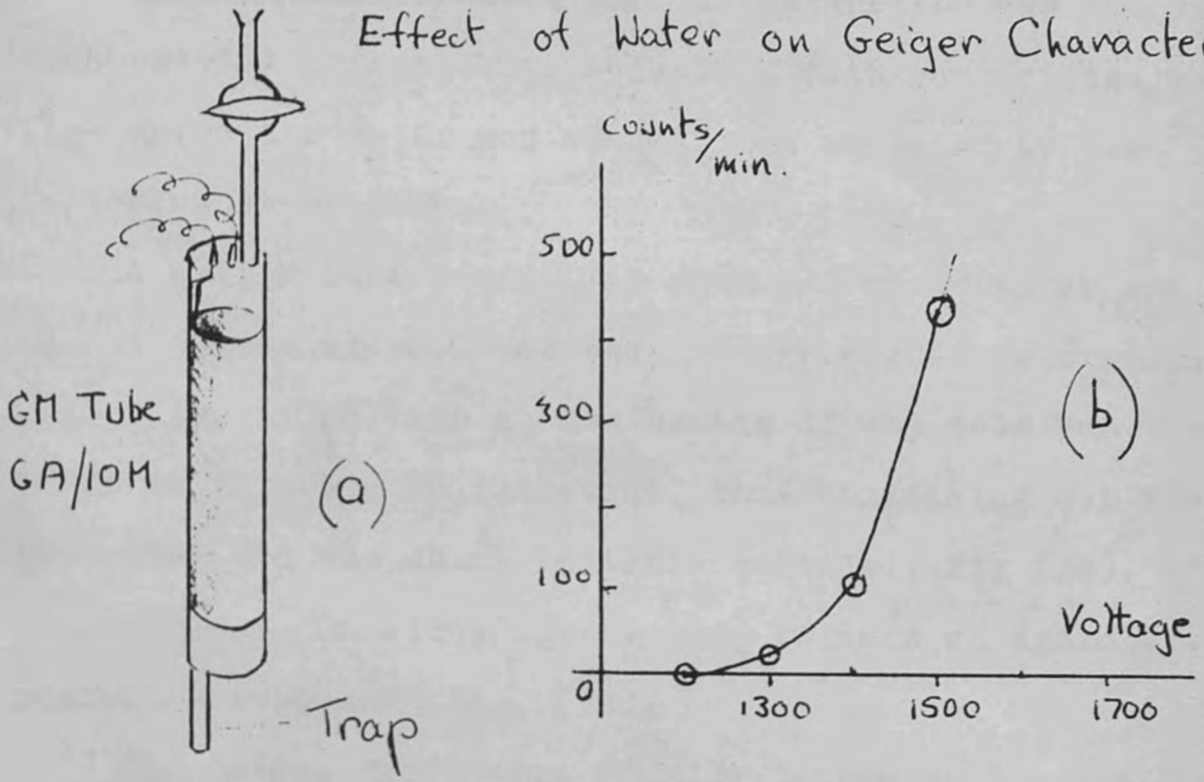
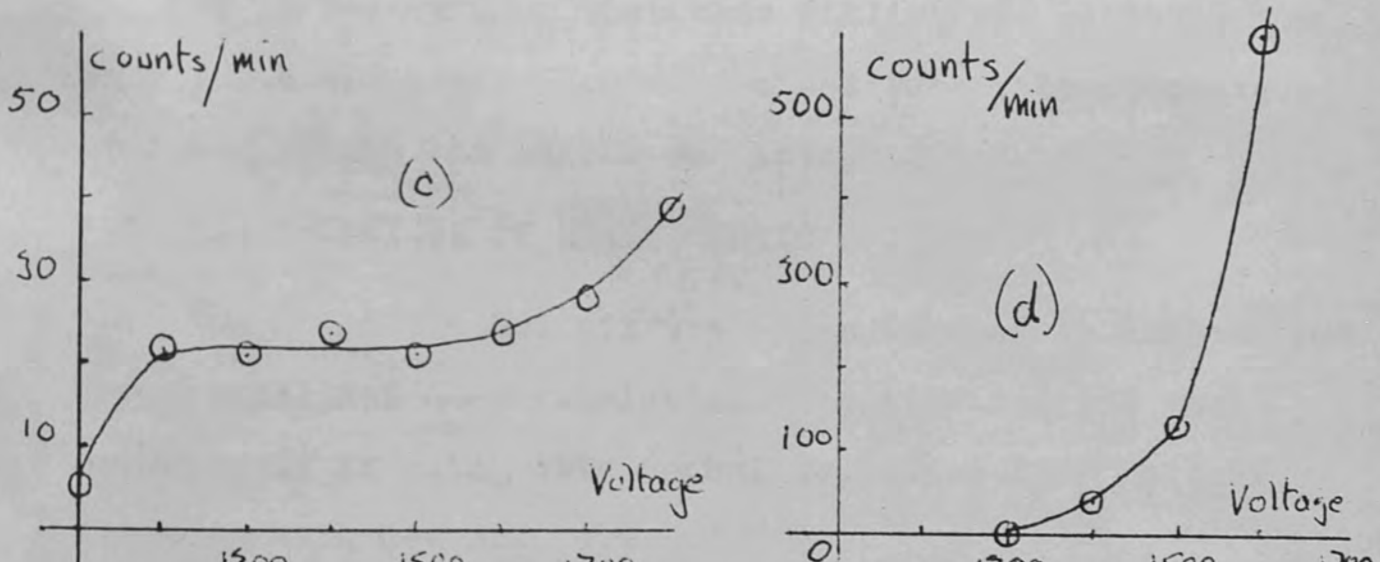


Figure (3)



Characteristics of Filling:- 9cms Argon. 1cm. Ethanol. 1cm Water

(b) Prior to immersion in coolant.

(c) 30 mins after immersion of trap in CO_2 - Acetone

(d) 2 hrs after removal of trap from coolant

The possibility that this deterioration was due to some trivial effect, e.g. a leak in that part of the vacuum line where the water was stored, was excluded by the following experiments.

A geiger tube was filled with 1.0 cm of water and 10 cms argon: alcohol and the characteristic determined Fig. (3b). The trap at the bottom of the tube was then immersed in solid CO_2: acetone, thus condensing out most of the water and the characteristic recorded, Fig (3c), after 20 minutes. On allowing the trap to warm up again the plateau disappeared Fig. (3d).

The geiger tubes were finally tested by Cameron who was also unable to obtain a plateau. He concluded that the tubes were faulty.

As it was evident that this filling was suitable for only a limited proportion of counter tubes, the technique of Black, Joris and Taylor was investigated.

(x) THE TECHNIQUE OF BLACK, JORIS & TAYLOR

The argon:alcohol mixture which is used in this method gives excellent characteristics. No difficulties were encountered in using this technique, apart from initial troubles with new counters.

The vacuum line required and the filling procedure adopted are essentially the same as in the preceding method.

In order to test the reliability of the technique it

Argon-Ethyl Alcohol Filling. Linearity between countrate and (a) Tritium Content + (b) Pressure

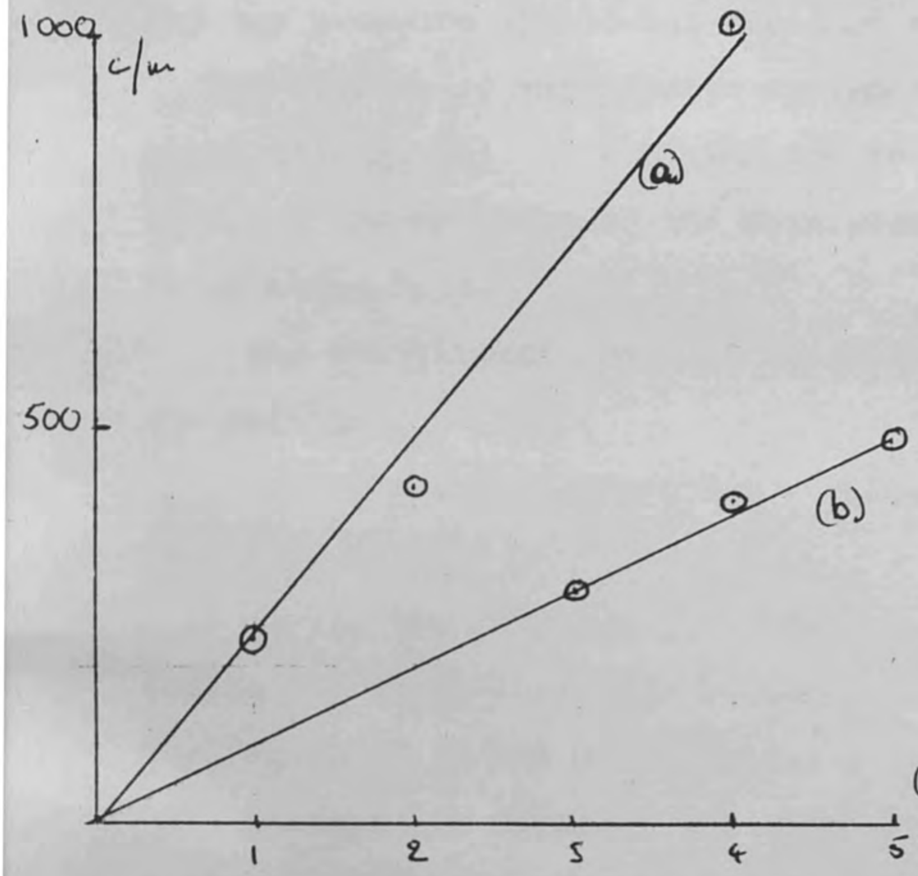


Figure (4)

(a) Concentration and (b) Pressure
Arbitrary Units.

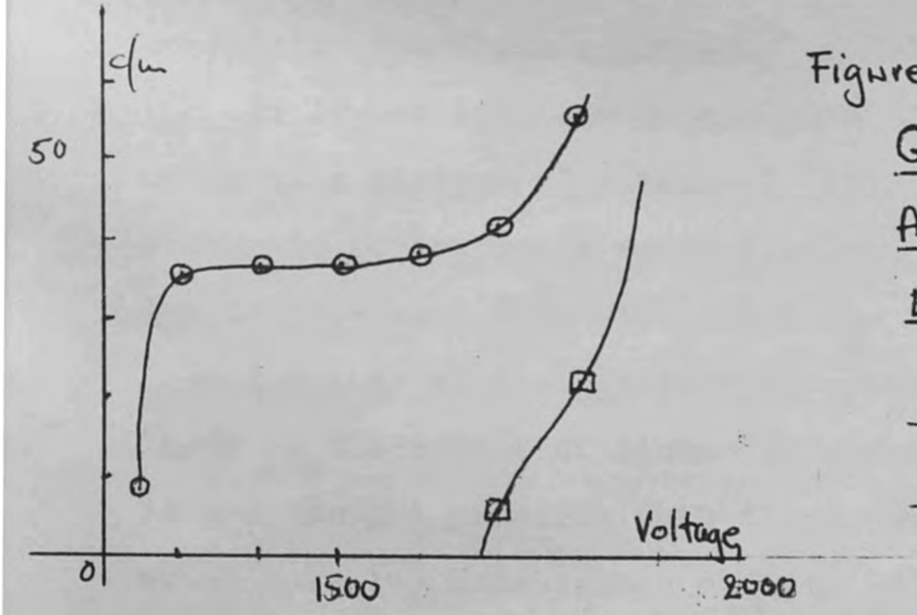


Figure (5)

Geiger Characteristic of Argon: Alcohol Fillings. Effect of Ethanol Pressure.

—⊙—⊙— 1cm EtOH. 10cm Argon

—□—□— 2cms EtOH. 10cm Argo

was necessary to establish the linearity of the relationship between count rate and (a) the activity of the alcohol and (b) the pressure of alcohol admitted to the counter.

The results of experiments designed to test this are shown in Fig. (4). Although the required linearity was observed the accuracy of the measurements was not very good, being about 7.5%.

The statistical error of these measurements based on the relation

$$\text{standard deviation} = \sqrt{\text{count/rate}}$$

is 1.25%.

It was thought that the rather large error might be due to the difficulty of accurately measuring pressures in the region of 10 mms on an ordinary manometer.

Attempts to increase the alcohol argon ratio caused a serious deterioration in characteristics Fig. (5), an observation which agrees with those of Spatz,[21] but which conflicts with those of Brown.[35]

As it was intended to estimate the weight of tritiated water in a mixture of water and dioxan it was essential either to separate the water from the dioxan quantitatively or to show that this separation was not necessary.

A survey of the literature revealed that nothing was known of the effect of dioxan on counting properties, but it was thought possible that dioxan even in small quantities would have two undesirable effects (a) on the geiger characteristic and (b) on the sensitivity of the filling.

These possibilities were disproved by experiment. It was found that fillings containing e.g. 8 mms alcohol, 4 mms dioxan and 130 mms argon had the same count rate as a mixture containing the same quantity of alcohol and no dioxan. The characteristics of the filling were, if anything, slightly improved.

It was therefore proposed that the proportion of active water mixed with dioxan would be determined by allowing the mixture to exchange with excess ethyl alcohol. The excess alcohol vapour would then be admitted to a counter tube and the count rate determined.

As the dioxan in the mixture was inactive, erroneously low results would be obtained unless the quantity of dioxan allowed to enter the counter was negligible.

The minimum excess of alcohol necessary was found experimentally. Samples containing various proportions of active ethyl alcohol and dioxan were prepared, and the activity of 12 mms of the vapour from each sample determined.

From the observed count rate the respective pressures of alcohol and dioxan in the counter tube were calculated. These results showed that a solution containing 10% by volume of dioxan reduces the count rate by 2.5%, i.e. about half the reduction which would be expected on the basis of Raoult's Law.

As the volume of dioxan collected in an average experiment would be less than .003 mls, the addition of 0.5 mls of ethyl alcohol would ensure that error from this source would be less than 0.15%.

Thus there seems to be no necessity to separate the dioxan from the water.

This procedure has the disadvantage of greatly diluting the activity of the sample so that only a small proportion of the total activity is measured.

However, as tritium is extremely cheap and highly active, the objections to diluting the tritium prior to analysis are theoretical rather than practical.

Furthermore diluting the sample has the advantage that the line can be flushed with the sample prior to counting and measurements can be repeated as often as required. As geiger tubes occasionally leak after filling, and sometimes unaccountably fail to function properly, the commitment of the whole of the sample to one counter, hazards several days work.

(xi) TRITIUM ASSAY AS HYDROGEN GAS

Although the preceding method was broadly satisfactory, it was thought that more accurate results would be obtained if a high pressure of tritiated gas or vapour could be introduced into the counter.

For this reason it was considered worthwhile to attempt

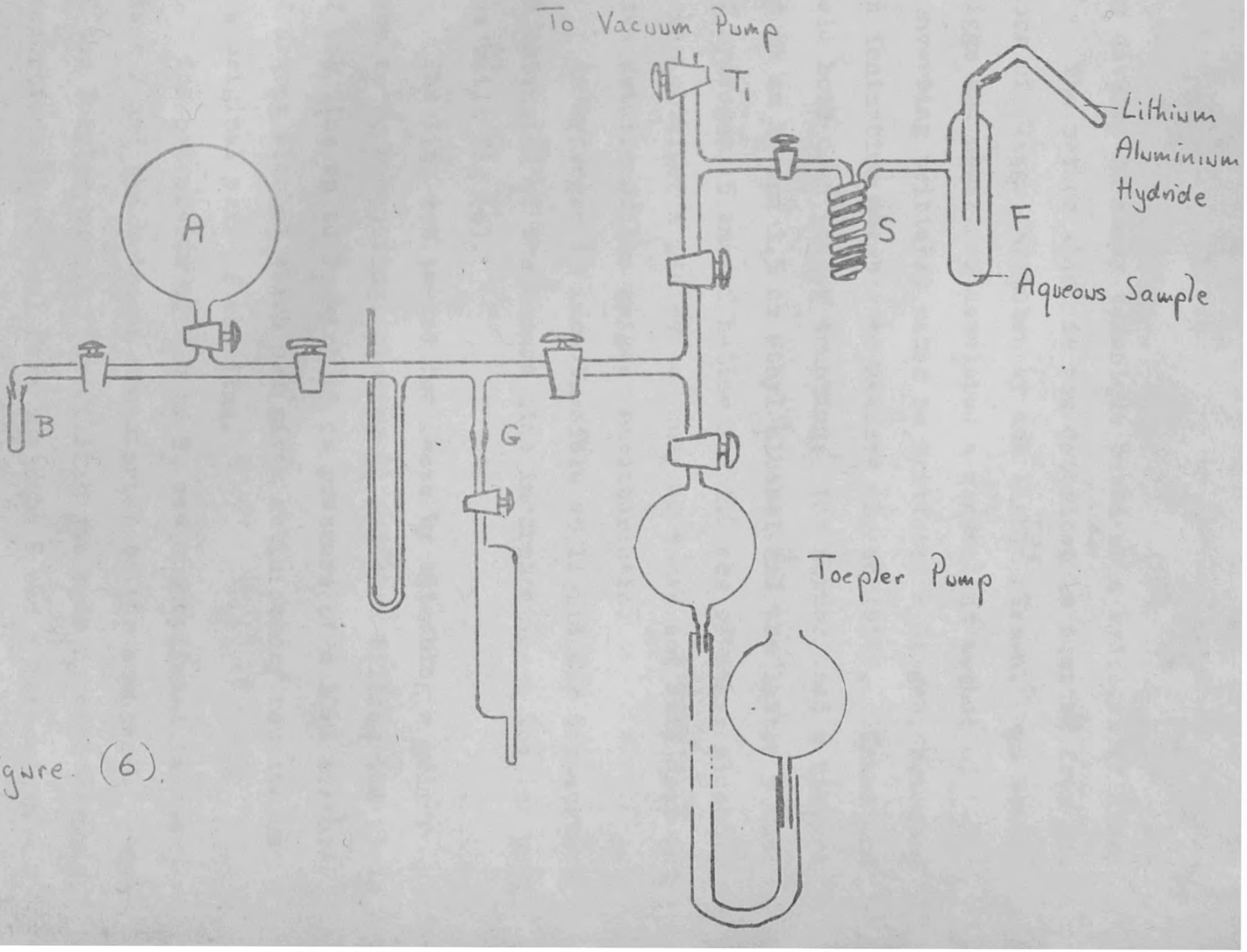

To Vacuum Pump
T_1
Lithium Aluminium Hydride
F
S
Aqueous Sample
A
B
G
Toepler Pump

Figure (6).

to develop an assay technique based on a hydrogen filling.

The method which is now described is adapted from the work of Biggs, Kritchensky and Kirk,[23] Kamen,[25] and Reid.[34] Biggs and coworkers developed a convenient method of converting tritiated water to tritiated hydrogen, but used an ionization chamber to measure the activity. Kamen and Reid both used geiger counting; the former used a mixture of 25 cm H_2 and 1.5 cm ethyl alcohol and the latter 9 cms of hydrogen, 5 cms of helium and 1.0 cms of ethyl alcohol. Kamen obtained a plateau of only 40 volts and Reid does not give details of the geiger characteristic.

As hydrogen is incondensible at liquid air temperature an extension of the vacuum line incorporating a Toepler pump was built Fig (6).

The line was tested for leaks by attaching a geiger tube to G, evacuating, closing T_1 and then filling the whole of the line up to T_1 with 10 cm pressure of a 10:1 mixture of argon: alcohol which had given satisfactory results on the original part of the line.

The conversion of H_2O to H_2 was accomplished in the flask F and the hydrogen transferred to the counter by means of the Toepler pump. The filling was made up with various proportions of alcohol from the tube B and a 20:1 argon - ethyl formate from the 5 litre flask A. The purpose of the spiral S which was cooled in liquid air, was to remove water vapour and other condensible impurities from the hydrogen.

Geiger Fillings containing Hydrogen.

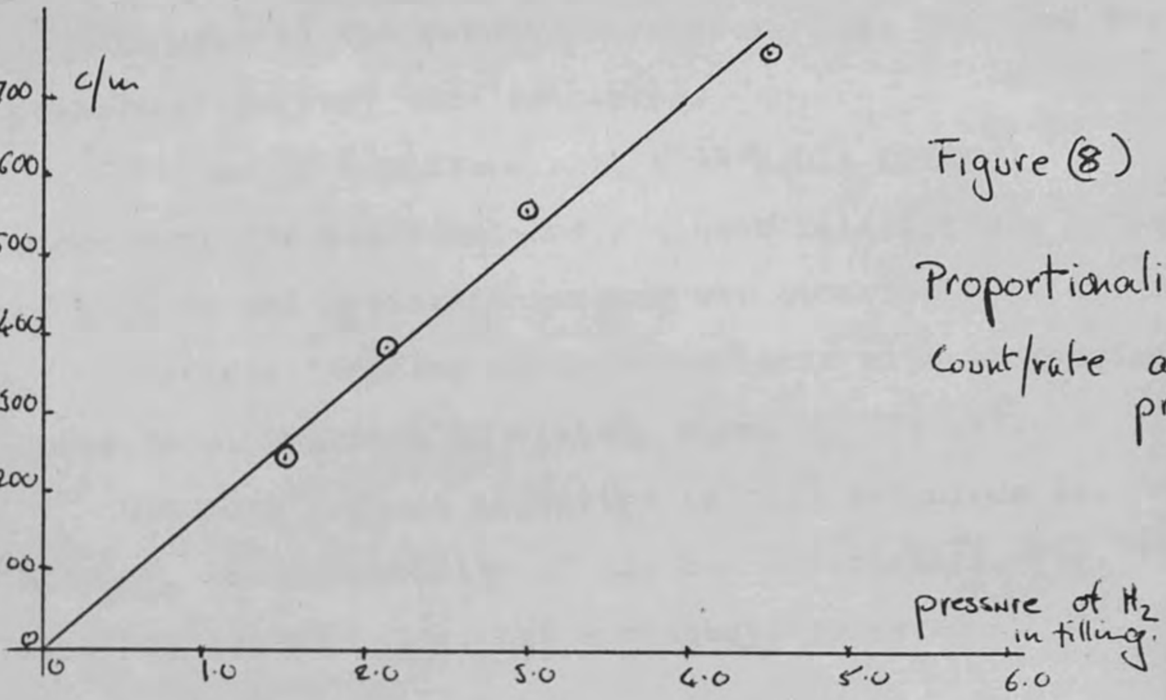
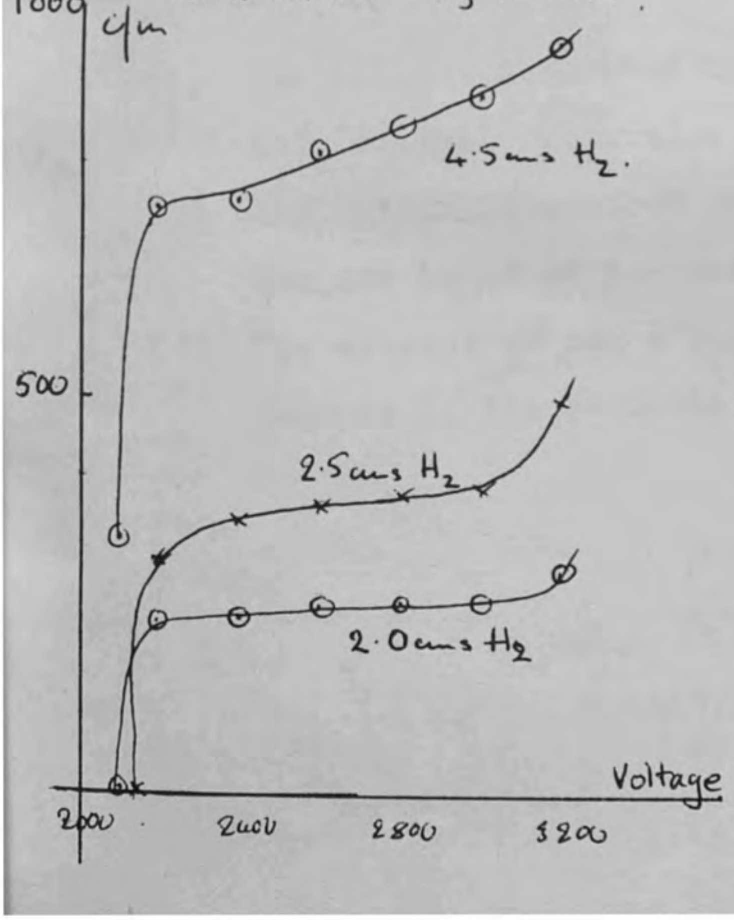


Figure (8)

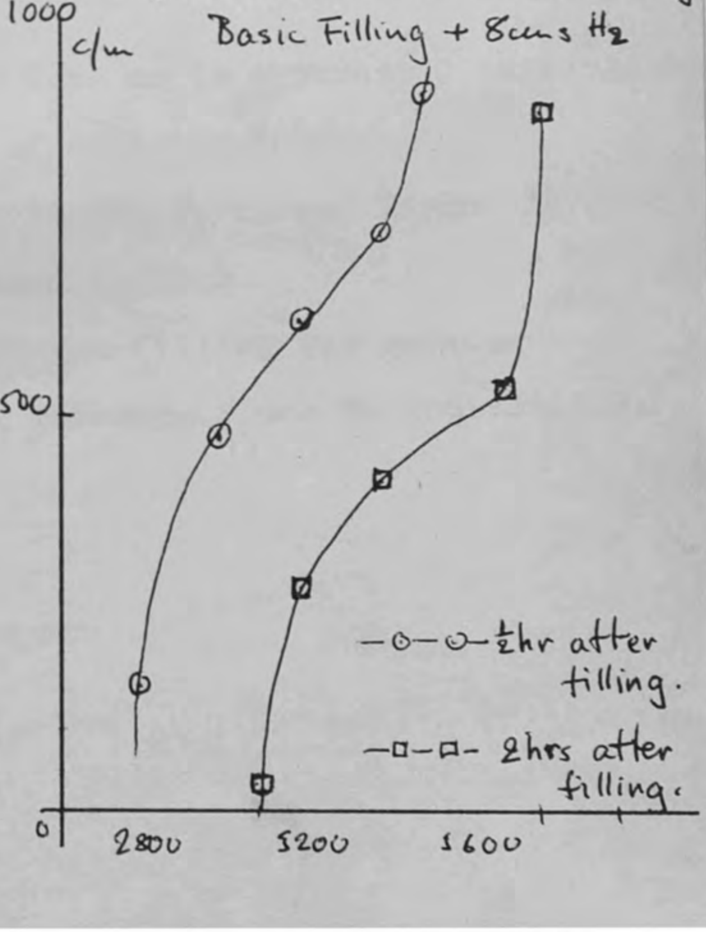
Proportionality of Count/rate against pressure.

Figure (9). Effect of Increasing H_2 Content.

Basic Filling:- 20cms Argon. 2cms Ethyl Formate. 1cm Ethyl Alcohol



Figure(7) Instability of Fillings



In general the results were poor, Fig. (7), and the procedure was very time consuming.

Eventually a mixture with a workable geiger characteristic was found and a linear relationship between count rate and hydrogen pressure was observed Fig (8).

The deterioration of characteristic with increasing pressure of hydrogen is clearly shown by Fig (9).

The most serious objection to this technique is, however, the instability of the characteristics, Fig. (7), which is occasionally, but not always observed.

Summary of Preliminary Work on Tritium Assay

None of the methods investigated was entirely satisfactory.

(1) The filling described by Cameron is apparently suitable for only a small proportion of counting tubes.

(2) The filling described by Black, Joris and Taylor is good but the error of the method is high.

(3) The attempt to use a hydrogen filling was unsuccessful because of the potential inaccuracy due to instability.

Geiger Characteristics of Ethyl Alcohol Fillings.

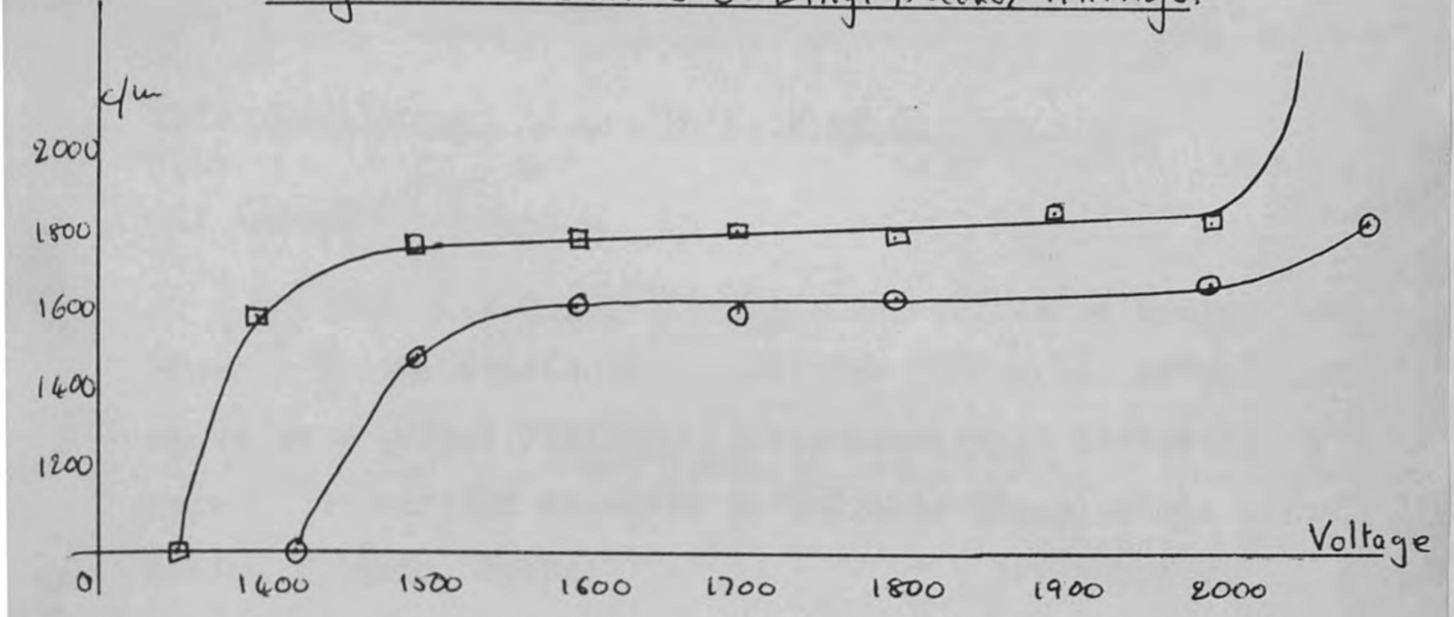


Figure (10)

Comparison of Characteristic of Ethyl Alcohol Filling with & without Argon.

		Plateau Length.	Slope/100v
—⊙—⊙—	1.0cm Ethyl Alcohol.	450 Volts	1.1 %
—⊡—⊡—	1.0cms Ethyl Alcohol + 10cms Argon	500 Volts.	0.9%.

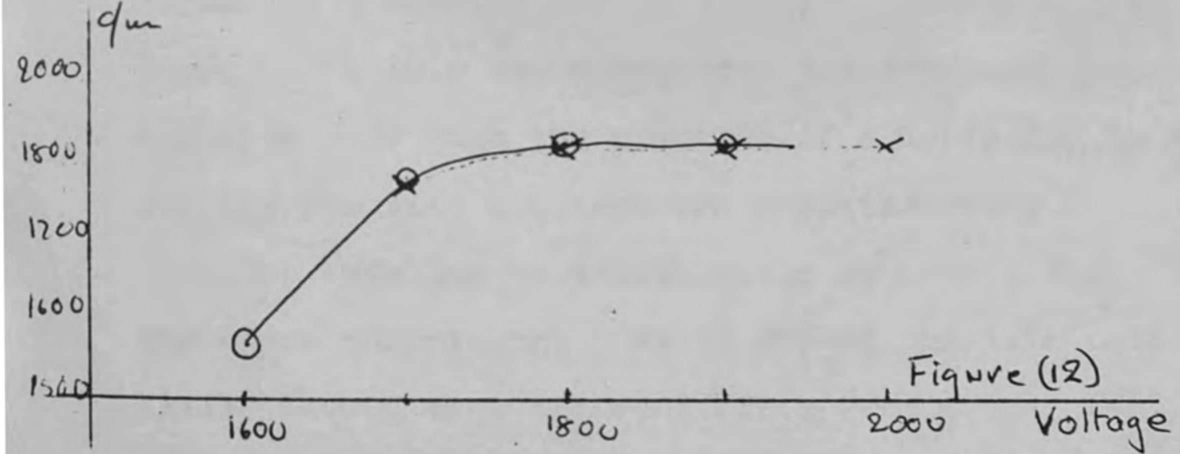


Figure (12)

Stability of Ethyl Alcohol Fillings.

-⊙—⊙- 7mins after filling
–x⋯x-- 28hours after filling.

A.

III. Development of New Methods of Tritium Assay

(i) ETHANOL

In view of the conflicting observations of Spatz[21] and Brown[35] on the effect of raising the proportion of quenching agent in a geiger filling, it was considered advisable to repeat the earlier attempts to increase the alcohol: argon ratio. Again, Spatz's observation of a deteriorating characteristic, which he tentatively attributed to oxygen dissolved in the alcohol, was confirmed.

The effect of varying the proportions of alcohol: argon was then studied more systematically, starting with a filling containing 10 cms of argon and no alcohol and in subsequent fillings increasing the pressure of alcohol from 0 to 3 cms.

Nothing of interest was observed until, to complete the sequence, a counter was filled with 1 cm of alcohol and no argon. A poor characteristic was expected, because it is commonly held that the presence of a noble gas is advantageous and low pressure fillings are unsatisfactory.[9b]

The excellent characteristic observed, Fig. (10), was therefore surprising. As it seemed possible that this filling would meet the need for a simple and rapid method of assay, the properties of the filling were thoroughly investigated.

The generality of the method was first established,

Ethyl Alcohol Fillings in the Absence of Argon.

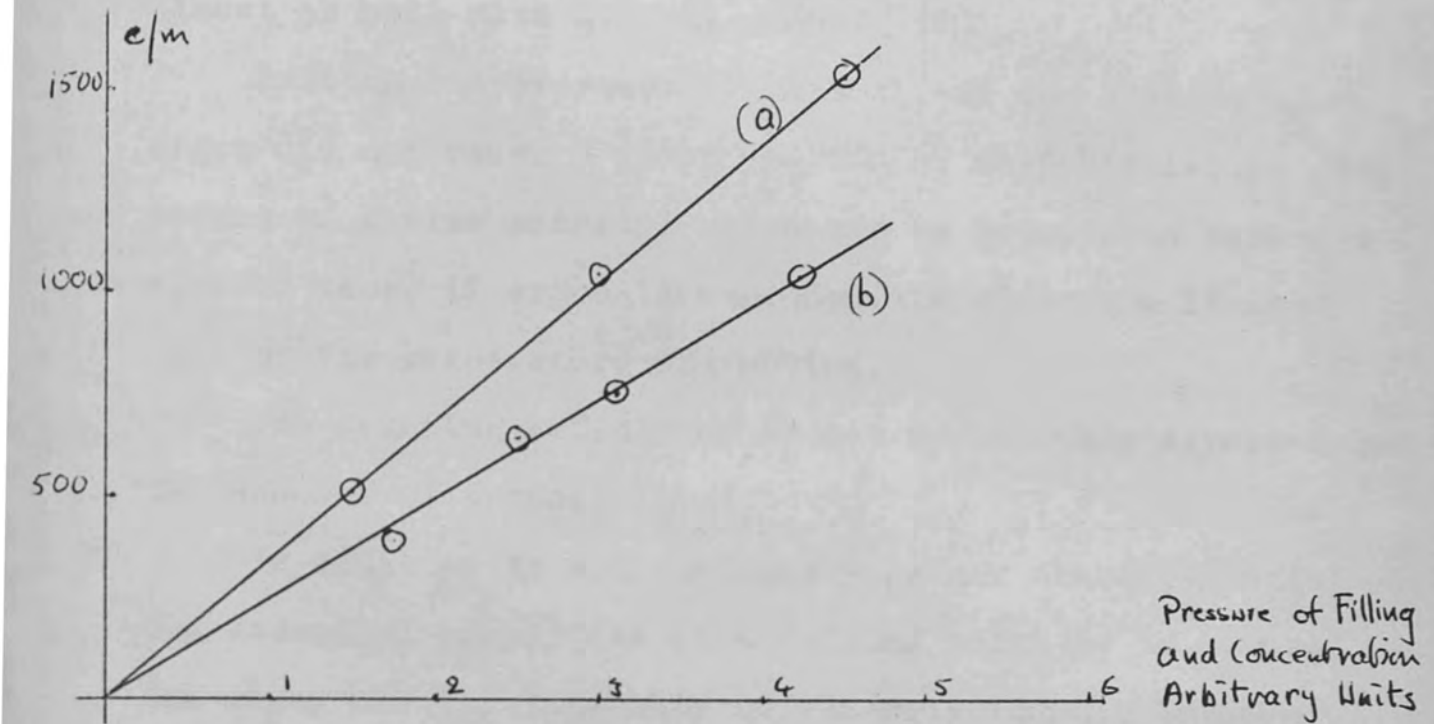


Figure (11). Relationship between count rate and (a) Tritium Content and (b) Pressure of Filling.

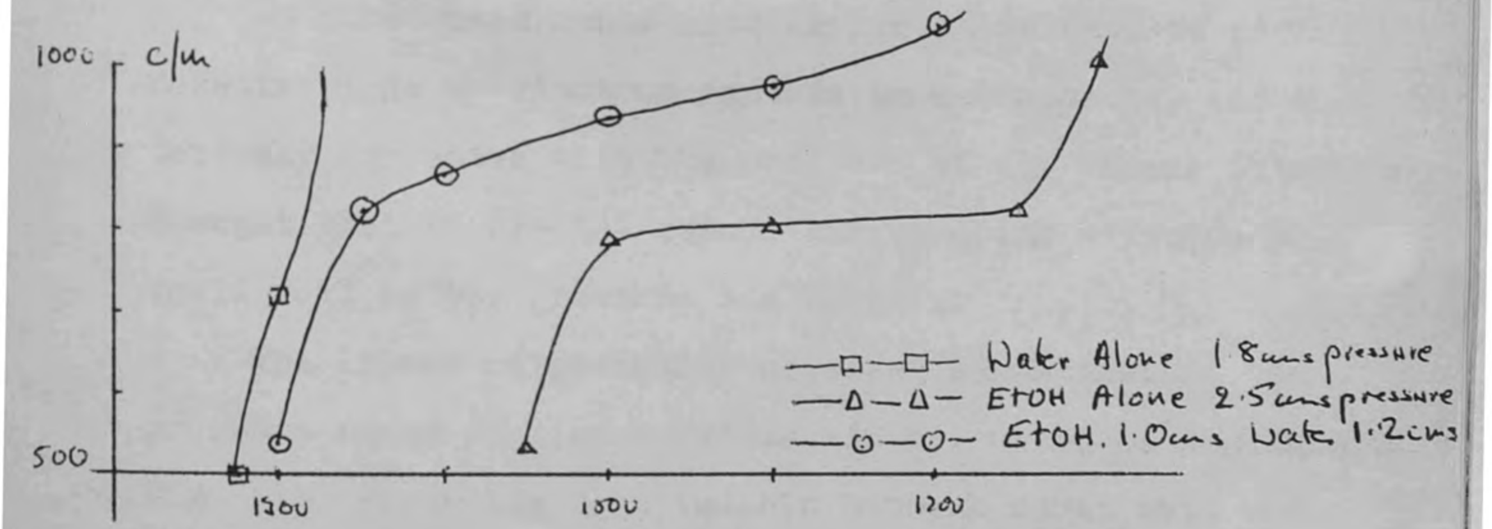


Figure (16) Effect of Water on Geiger Characteristic of Ethyl Alcohol Fillings i.e. it was found that any geiger tube, which gave satisfactory plateaus with argon: alcohol, would function almost as well with alcohol alone.

Raising the pressure of alcohol, in the absence of argon did not cause a deterioration of characteristic. The amount of active material which can be introduced into the counter tube, if argon is excluded, is therefore limited only by the temperature of counting.

The counting efficiency is not appreciably affected by the absence of argon.

In addition to a satisfactory geiger characteristic the essential properties of a filling which is to be used for assay are (1) linearity of the relationship between observed count rate and the pressure of tritiated vapour (2) between observed count rate and the activity of the tritiated alcohol and (3) stability.

As substances containing oxygen atoms tend to form negative ions by electron capture in a discharge, and this tendency increases with the pressure of the vapour it was thought that in alcohol vapour the counting efficiency would fall as the pressure was raised.

The linear relationship observed shows that in the pressure range studied negative ion formation is negligible. Fig. (13) shows the relationship between count rate and activity, from which the accuracy of the method is estimated to be ± 2%.

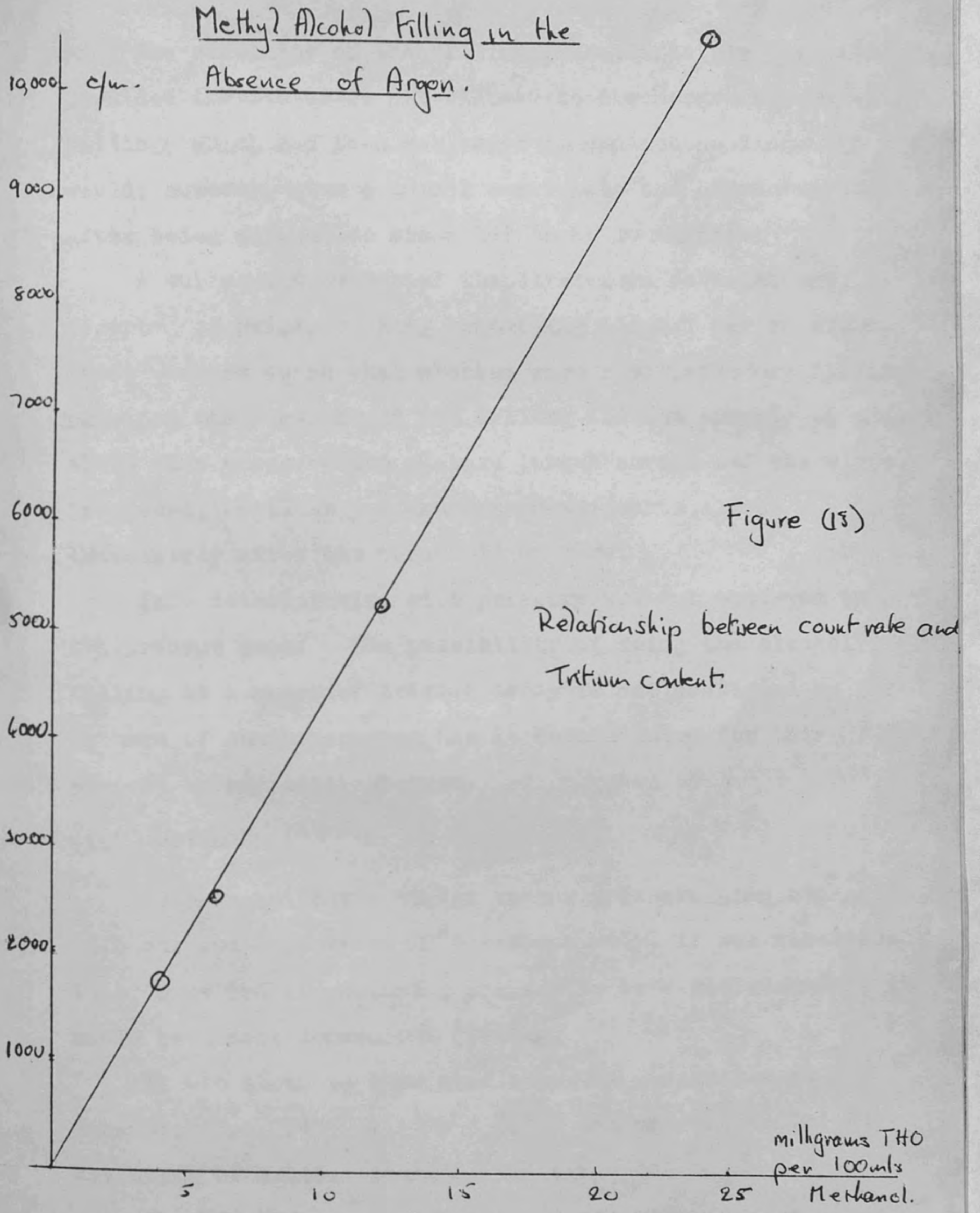


Figure (18)

Relationship between count rate and Tritium content.

The stability of the filling is satisfactory Fig (12) provided the counter is not allowed to discharge continuously. Fillings which had been subjected to continuous discharge would, however, give a normal count rate and characteristic after being allowed to stand for about 15 minutes.

A subsequent search of the literature revealed one report[39] of geiger filling containing alcohol but no argon. These workers found that alcohol gave a satisfactory filling provided the pressure of the filling did not exceed 4.5 cms. Above this pressure the plateau length shrank and the slope increased, until at 5.5 cms breakdown starts almost immediately after the threshold voltage.

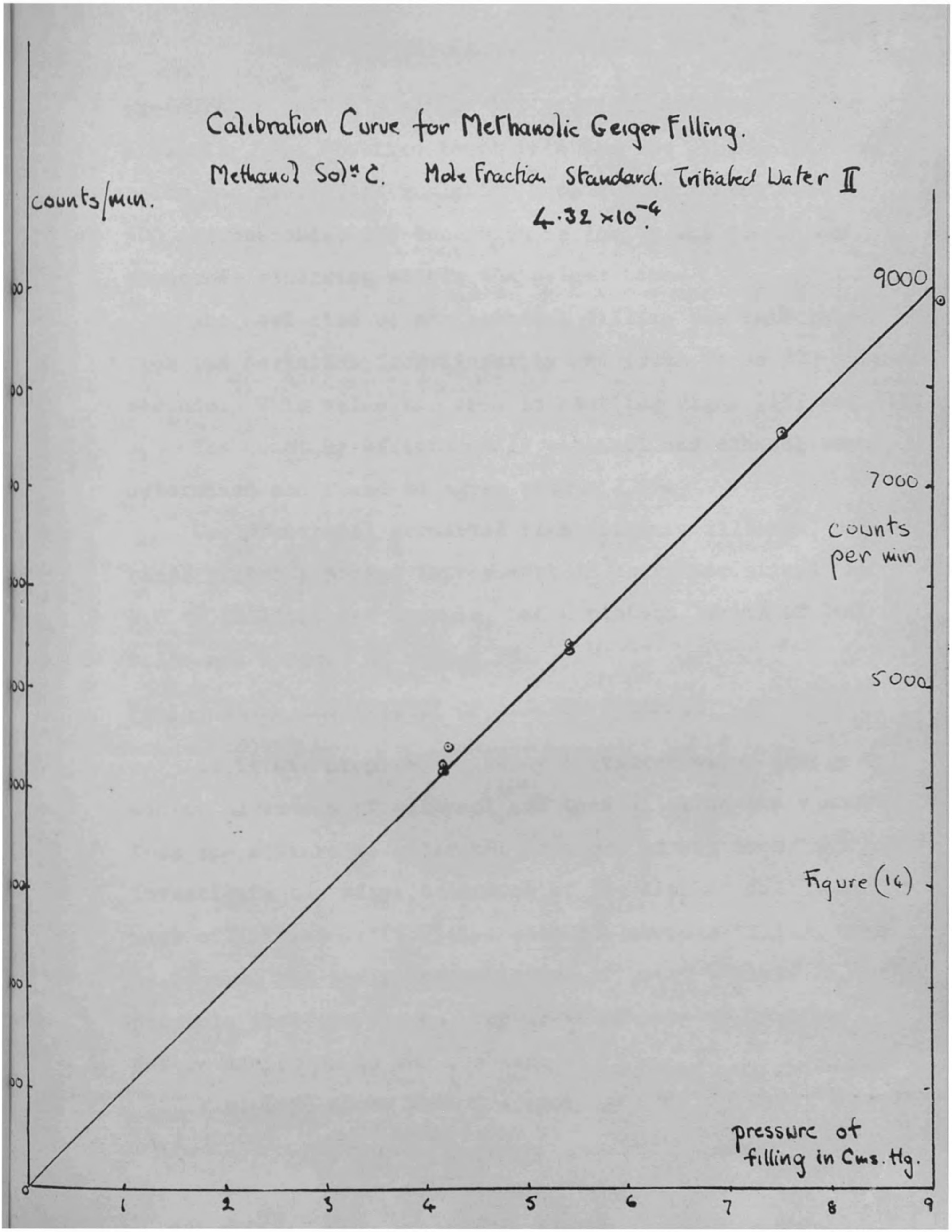
This deterioration with pressure was not observed in the present work. The possibility of using the alcohol filling as a means of tritium assay is not mentioned by the authors of the paper, nor has it been adopted for this purpose by any other workers.

(ii) METHANOL

As methanol has a higher vapour pressure than ethanol (9.6 cms and 4.3 cms at 20°C respectively) it was considered that, provided its counting properties were satisfactory, it would be a more convenient filling.

It was shown to have much the same properties as ethanol, Figs. (13), (14) and (17), and had the additional advantage of a lower starting voltage.

The plot of count rate against activity, and against



Calibration Curve for Methanolic Geiger Filling.

Methanol Sol^n C. Mole Fraction Standard. Tritiated Water II 4.32×10^{-4}.

Figure (14)

pressure, revealed a slight but systematic deviation from linearity, the observed count rate for the high activities being too low. This indicates a dead time longer than 300 microseconds, and thus must be due to the discharge processes occurring within the geiger tube.

The dead time of the methanol filling was calculated from the deviation from linearity and found to be 500 microseconds. This value was used in plotting Figs. (13) and (14).

The counting efficiency of methanol and ethanol were determined and found to agree within 2.8%.

Use of methanol permitted high pressure fillings, and these showed a marked improvement in characteristics. An 8.0 cm filling, for example, had a plateau length of 1000 volts and a slope of only 0.5%.

(iii) WATER SENSITIVITY OF ALCOHOL FILLINGS

As it was proposed to assay tritiated water simply by adding an excess of methanol and then allowing the vapour from the mixture to enter the counter, it was important to investigate the water tolerance of the alcohol fillings. In view of initial difficulties with the aqueous filling used by Cameron and the recommendations of other workers it seemed possible that the alcohol vapour would have to be dried before admission to the counter.

Fig. (15) shows that the admission of 25% water vapour

Methyl Alcohol Fillings

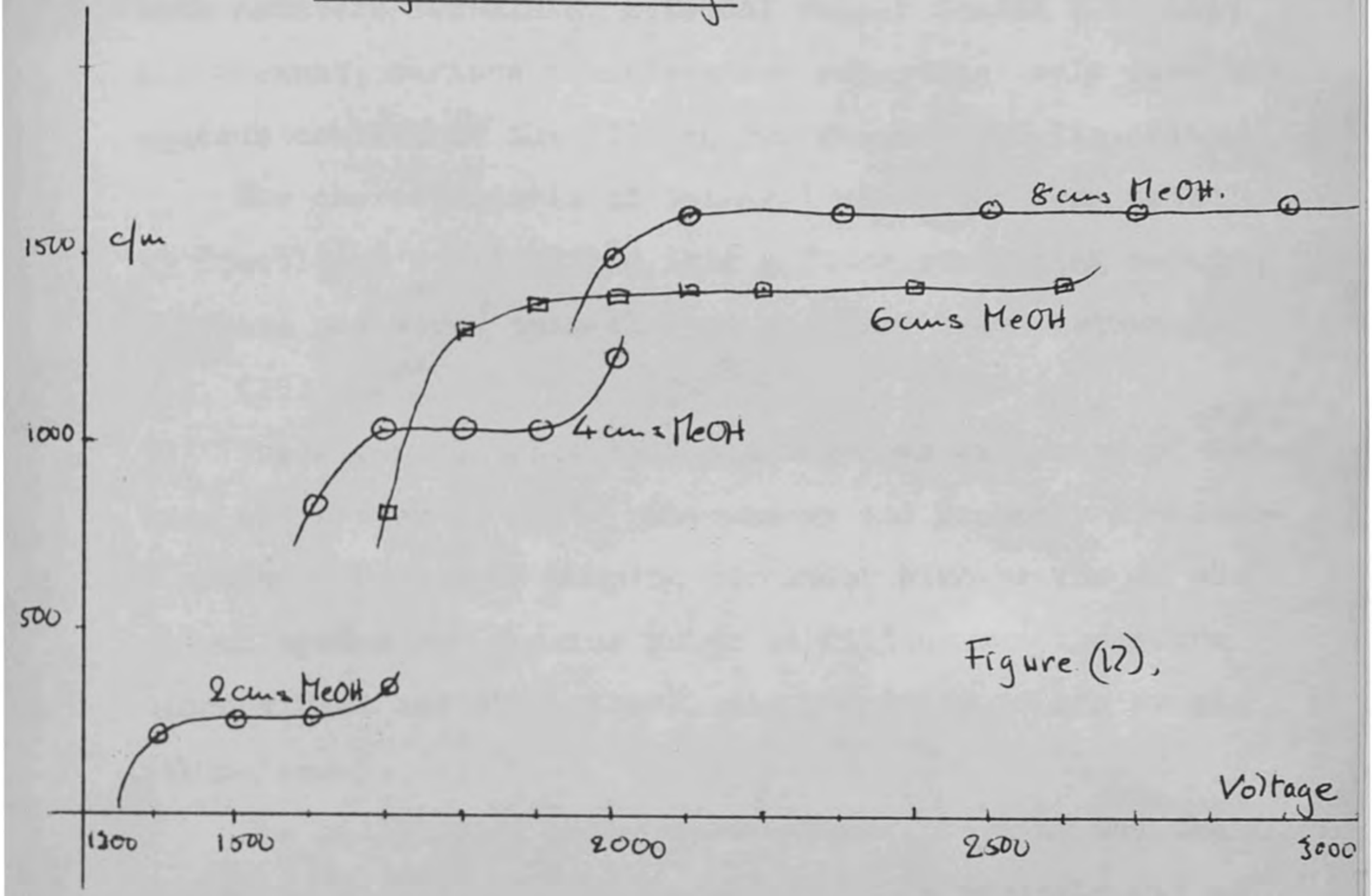


Figure (12),

Effect of Increasing pressure of filling.

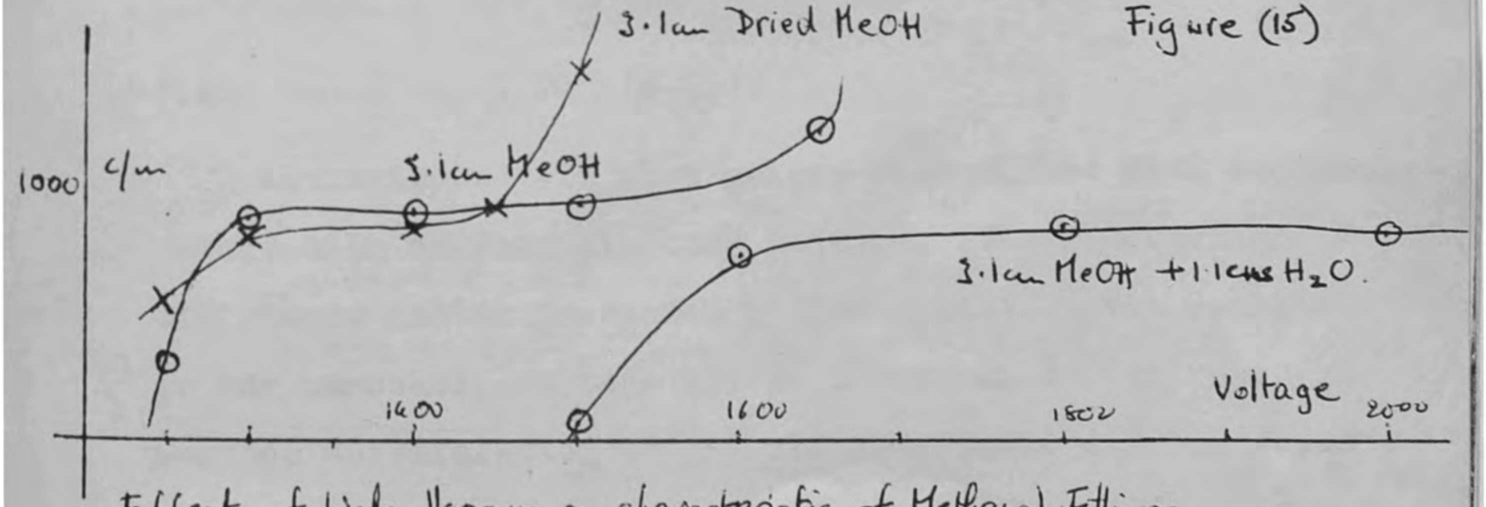


Figure (15)

Effect of Water Vapour on characteristic of Methanol Fillings.

into counters containing methanol vapour showed a similar improvement, serious deterioration occurring only when the aqueous content of the filling had reached 50% Fig. (16).

The characteristic of methanol which had been dried by fractional distillation into a flask containing calcium sulphate was worse than that of ordinary bench methanol Fig. (15).

These results show that the rigorous exclusion of water from the system is quite unnecessary and probably disadvantageous. Prolonged pumping out under high vacuum of the vacuum system and counter prior to filling was therefore discontinued and the methanol was not dried at any stage during assay.

The addition of water to a methanol filling had the following additional effects on the characteristic (i) an increase in the starting voltage (ii) a slower approach to breakdown and (iii) a slight lowering of the counting efficiency.

(iv) SENSITIVITY TO AIR

Admission of air to a geiger tube filled with methanol resulted in a lower starting voltage, a higher counting efficiency and an increased plateau slope. The approach to the threshold voltage and to breakdown was sharper. Serious deterioration of the characteristic did not occur until the air content reached about 50% Fig. (18). It was

Methyl Alcohol Fillings

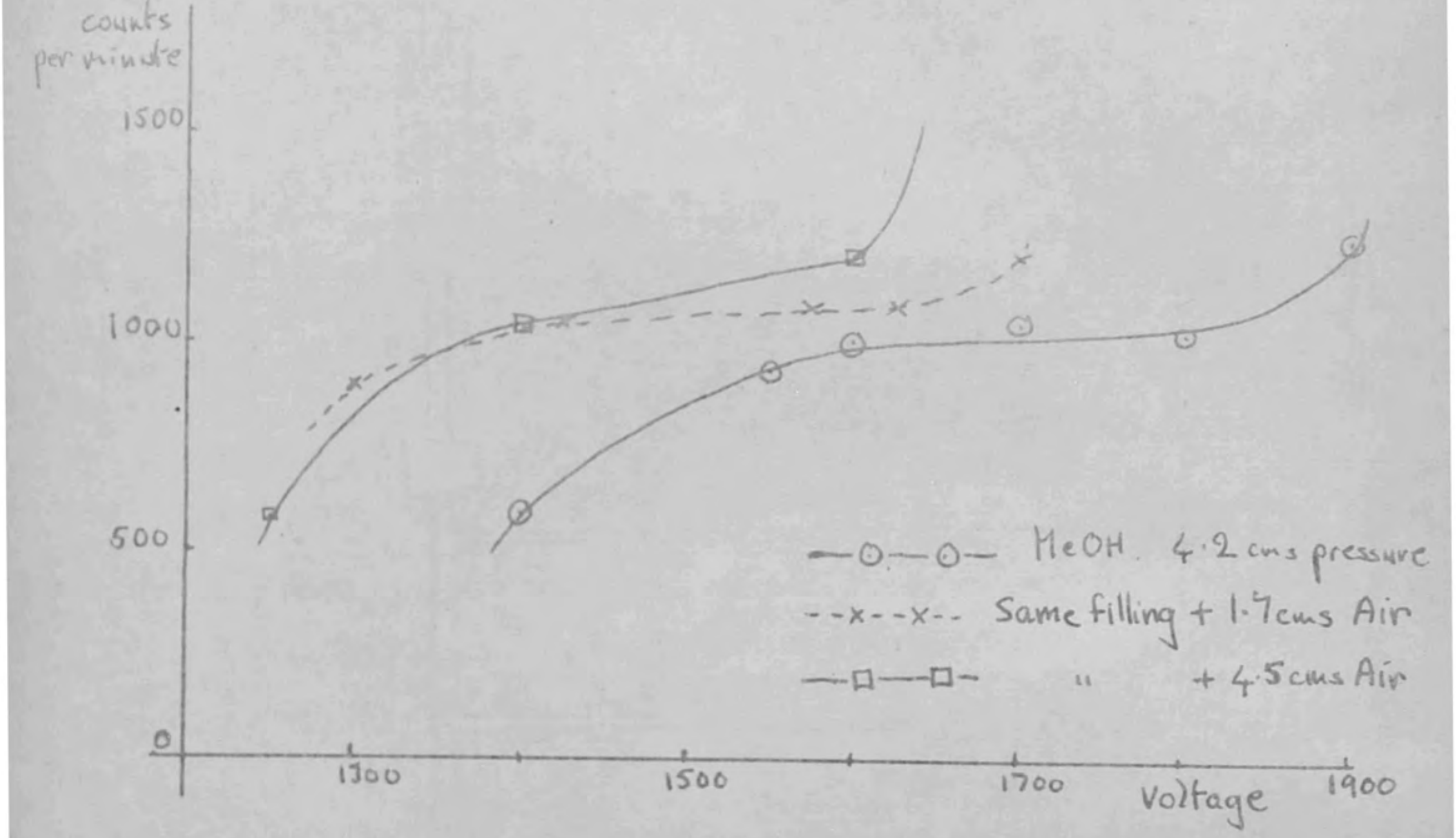


Figure (18) Effect of Air on Characteristic

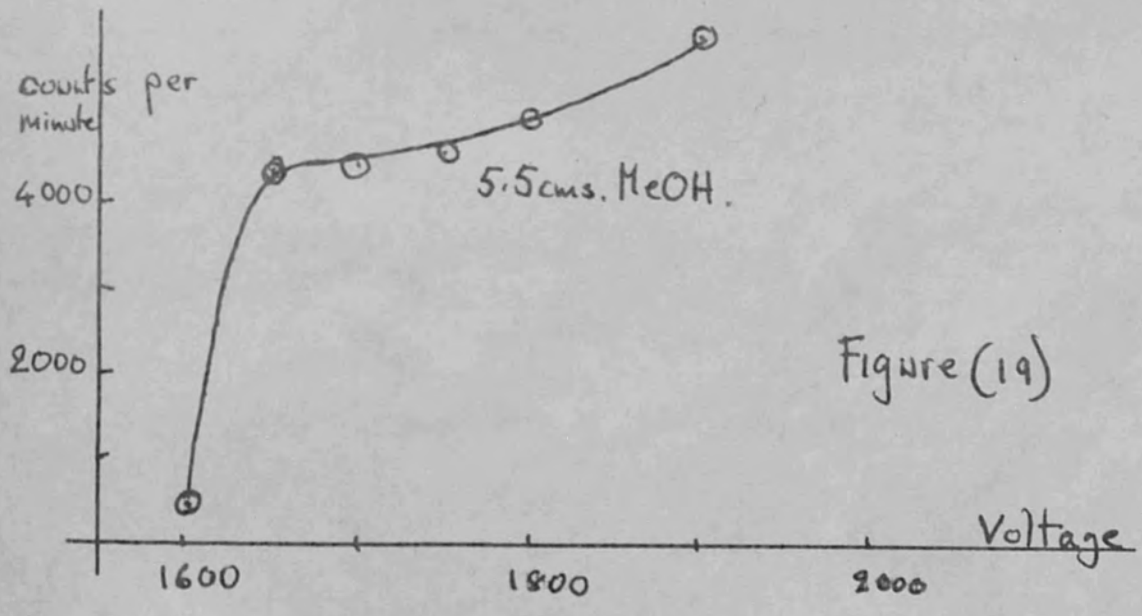


Figure (19)

Characteristic using Vacuum line operated by water pump only.

Simple Vacuum Line for Approximate Tritium Assay.

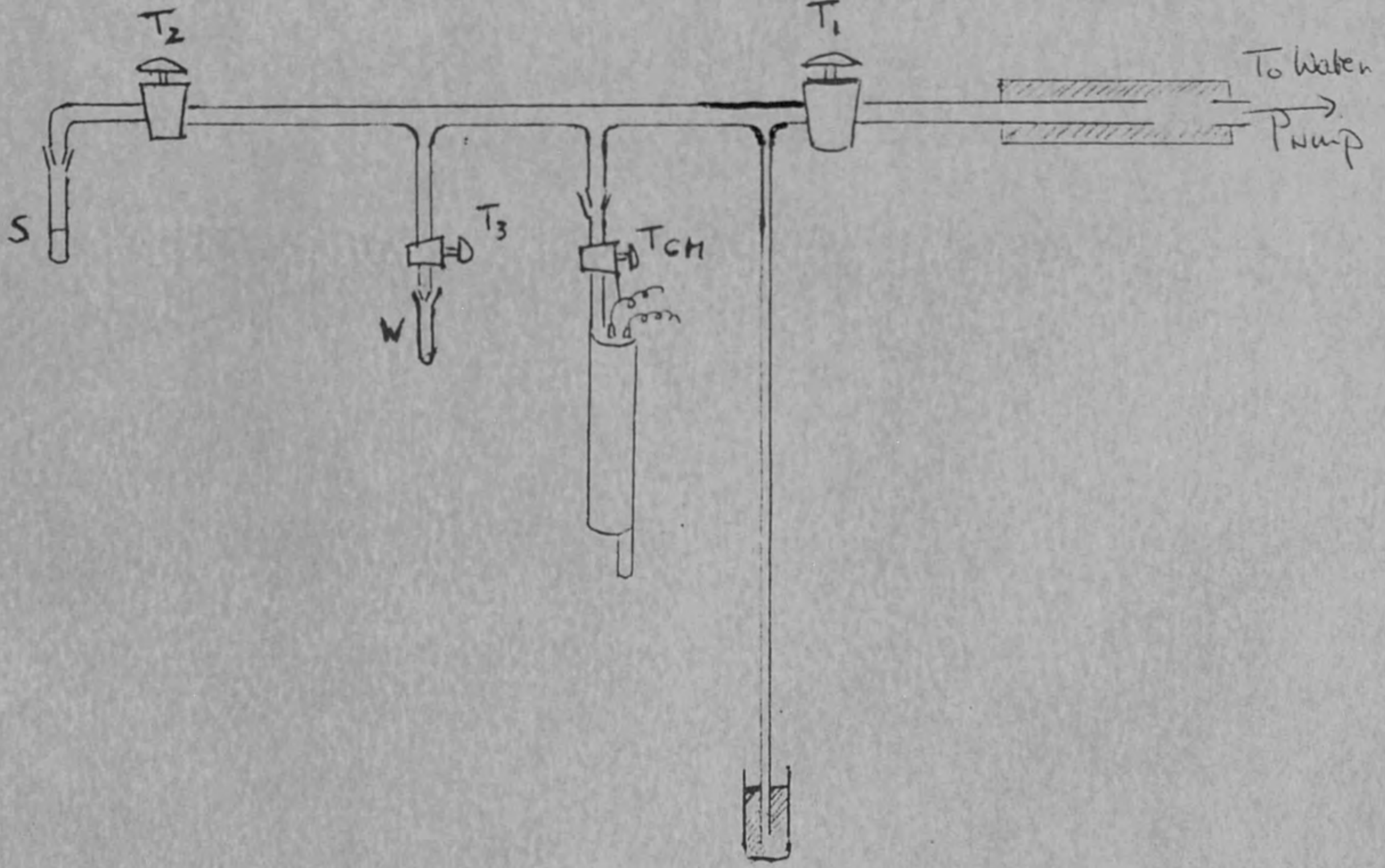


Figure (29)

clear from this that a modest pumping system would be adequate for filling a geiger tube. The characteristic shown in Fig. (19), having a plateau length of 150 volts and a slope of only 9% was obtained using the simple vacuum line in Fig. (29). A water pump was the only source of vacuum. The tube W was cooled in liquid air prior to filling the counter with the sample S, T_1, T_2 and T_{gm} being closed. This removed most of the inactive water vapour from the pump.

The marked reduction of starting voltage which was found to accompany the admission of air to a filling proved useful in enabling leaking tubes to be recognized and rejected. The importance of rejecting leaking tubes is shown by Fig. (18) from which it is seen that a leakage of air may be too small to affect seriously the plateau slope, yet sufficiently large to increase the counting efficiency. If such a tube were not detected a spuriously high count rate would be recorded.

(v) PRECAUTIONS

A puzzling feature of the geiger characteristic sometimes observed in early work with alcohol fillings was a "hump" at the beginning of the plateau followed by a negative slope Fig. (20). Similar characteristics were recorded, without explanation, by Jackson and Lampe[36] when working with a filling containing 99% helium and 1%

Alcohol Fillings

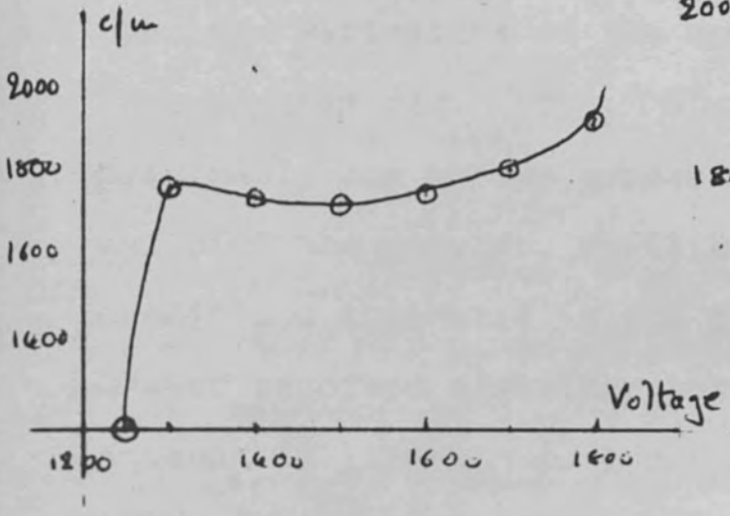


Figure (20). Geiger Characteristic of Alcohol Filling Immediately after filling.

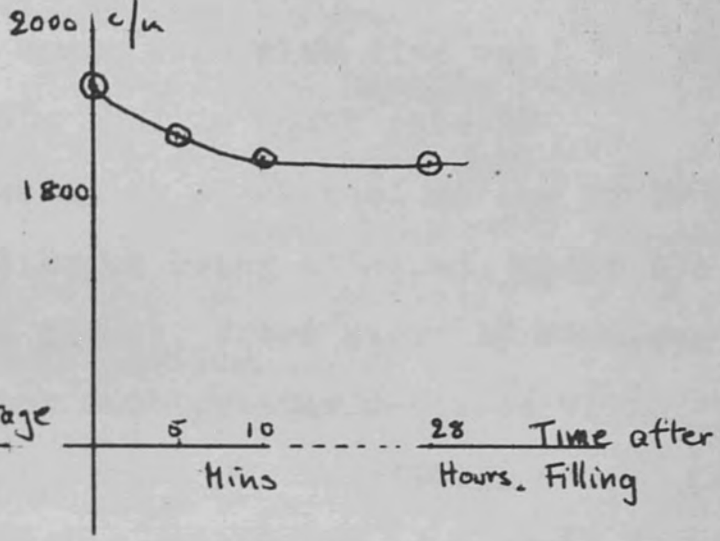


Figure (21). Fall of count rate with time after filling.

Acetone Filling

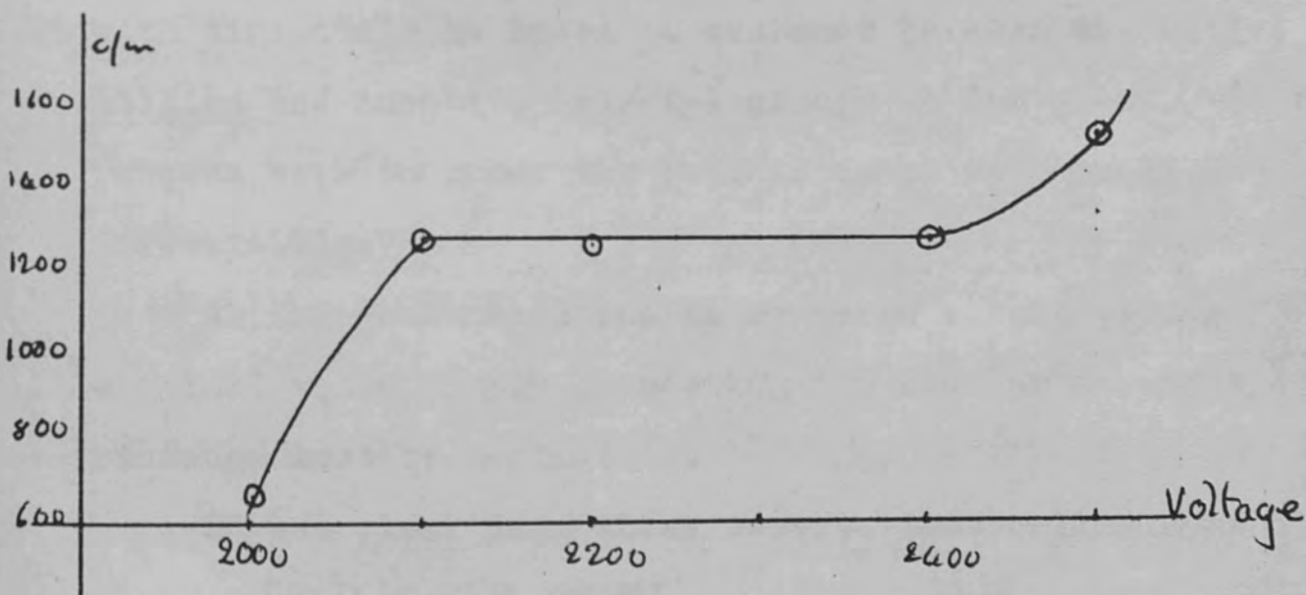


Figure (27). Geiger Characteristic. 5cms pressure of Acetone.

isobutane.

The explanation for this behaviour was found later when the variations of the count rate with time was investigated Fig. (21). The fall in count rate is presumably due to the condensation of alcohol on the inner walls of the counter, equilibrium being attained, under the conditions indicated in the figure, after about 10 minutes. Drever reported a similar but much greater decrease with aqueous fillings. As condensation of the alcohol does not reduce the amount of tritium within the counter it is not immediately obvious that condensation should reduce the count rate. This follows from the low energy of tritium radiation, particles originating in an adsorbed layer of alcohol remote from the sensitive region of the counter having only a low probability of detection.

An alternative explanation of the fall of count rate with time could be based on exchange between the active filling and inactive hydroxyl groups in the glass. If this process were to occur the fall in count rate would be irreversible.

As the count rate can be restored almost to its original value simply by heating the counter at about 38°C, exchange must be negligible.

It was clear from these results that reliable results would not be expected unless some procedure to allow for, or counteract, this condensation was evolved.

The problem was solved by wrapping a heating tape round the lead castle and maintaining the latter at a temperature of about 35°C by simmerstat.

Geiger tubes were inserted in the lead castle immediately after filling and allowed to warm up for at least ten minutes before counting.

It was confirmed by experiment that the count rate was not affected by temperature provided the latter was above the minimum necessary to prevent condensation.

(vi) WATER

Satisfactory characteristics having been observed with methanol and ethanol in the absence of argon, it was of interest to see if water would be a suitable filling under the same conditions.

First attempts were completely unsuccessful, but it was subsequently found that the characteristics were greatly improved by heating the counter Fig (22). The improvement in characteristic is accompanied by the disappearance of the multiple pulses which are typical of geiger fillings containing a high proportion of water at room temperature.

Raising the temperature presumably removes adsorbed layers of water from sensitive parts of the counter which is then able to function normally. The improvement may

Geiger Fillings Containing Water Alone.

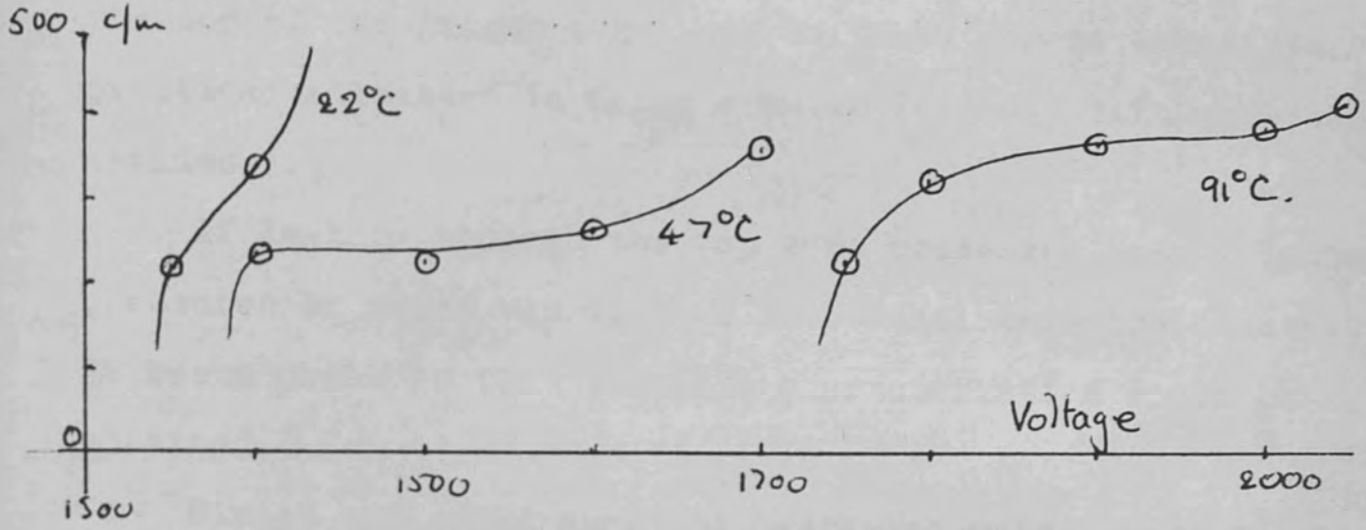


Figure (22) Effect of Temperature on Characteristic of GM Tube containing 2cms. pressure of water

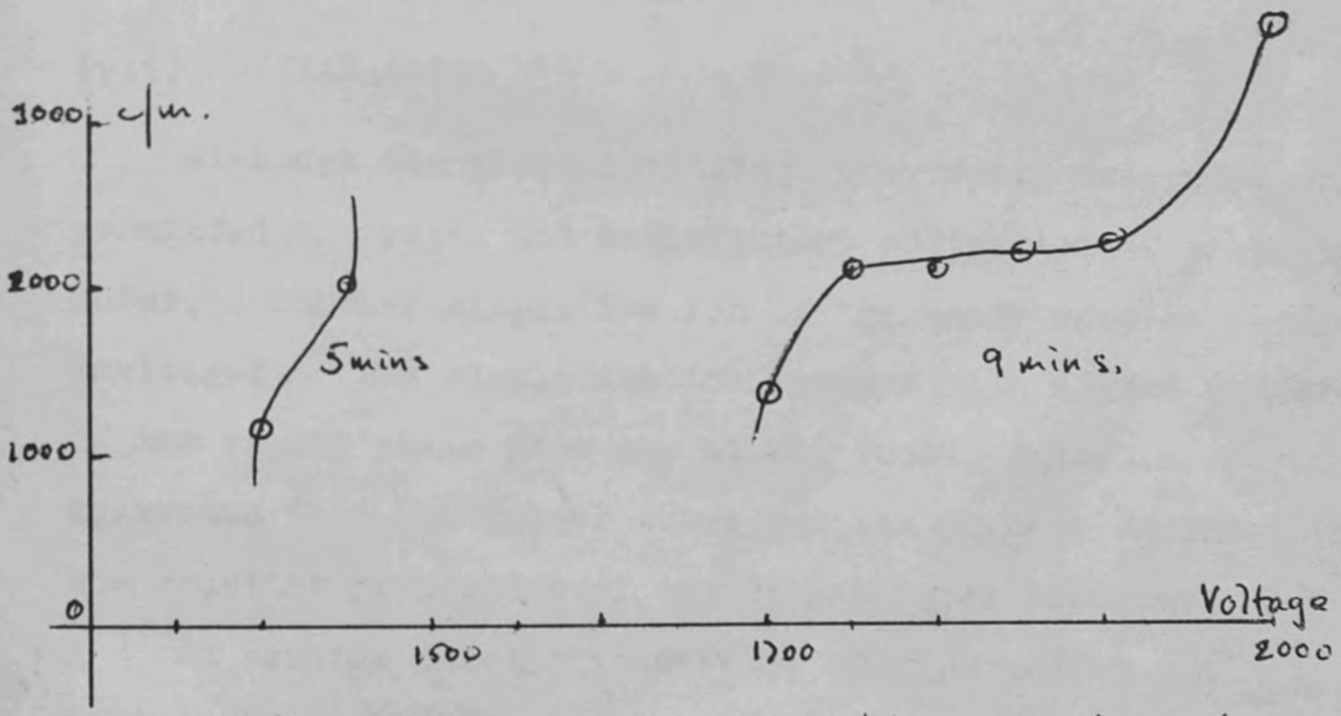


Figure (21). Change of Characteristic on standing in Lead Castle heated to 43°C.

also be due to the increase in pressure accompanying higher temperatures.

Some difficulty was experienced in counting at high temperatures due to leakage through the melting grease on the top of the geiger tube, and as there was no immediate practical advantage in using a water filling, this work was abandoned.

If leakage through the top were prevented and if higher pressures of water vapour were introduced into the counter, it seems probable that workable characteristics would be obtained.

Direct and rapid assay of tritiated water using very simple apparatus would then be possible.

Fig. (23) illustrates the sharpness of the change of characteristic which occurs on heating.

(vii) DIOXAN-WATER

Although the alcohol fillings previously described permitted the rapid and satisfactory estimation of tritiated water, a further simplification of the assay problem was envisaged. The simplification involved the direct transfer of the vapour phase from the static vapour pressure apparatus into the geiger tube; and its success depended on the counting properties of the dioxan-water mixture.

An earlier attempt to develop this procedure had failed, because at that stage the presence of argon as a

Dioxan-Water Fillings

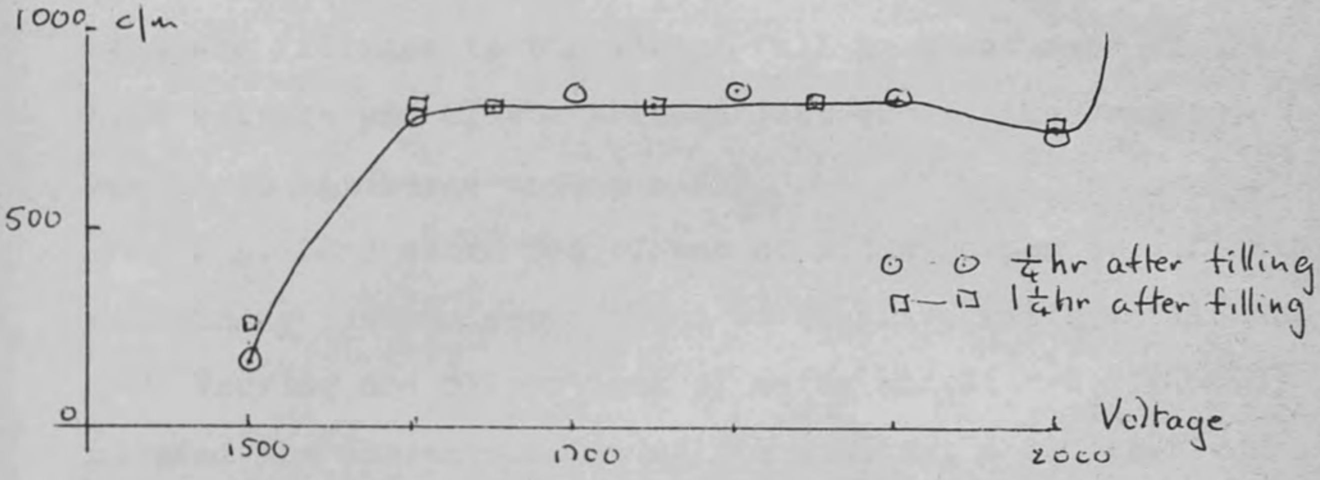


Figure (24) Geiger Characteristic of 4.3cms Vapour From 6% Aqueous Dioxan.

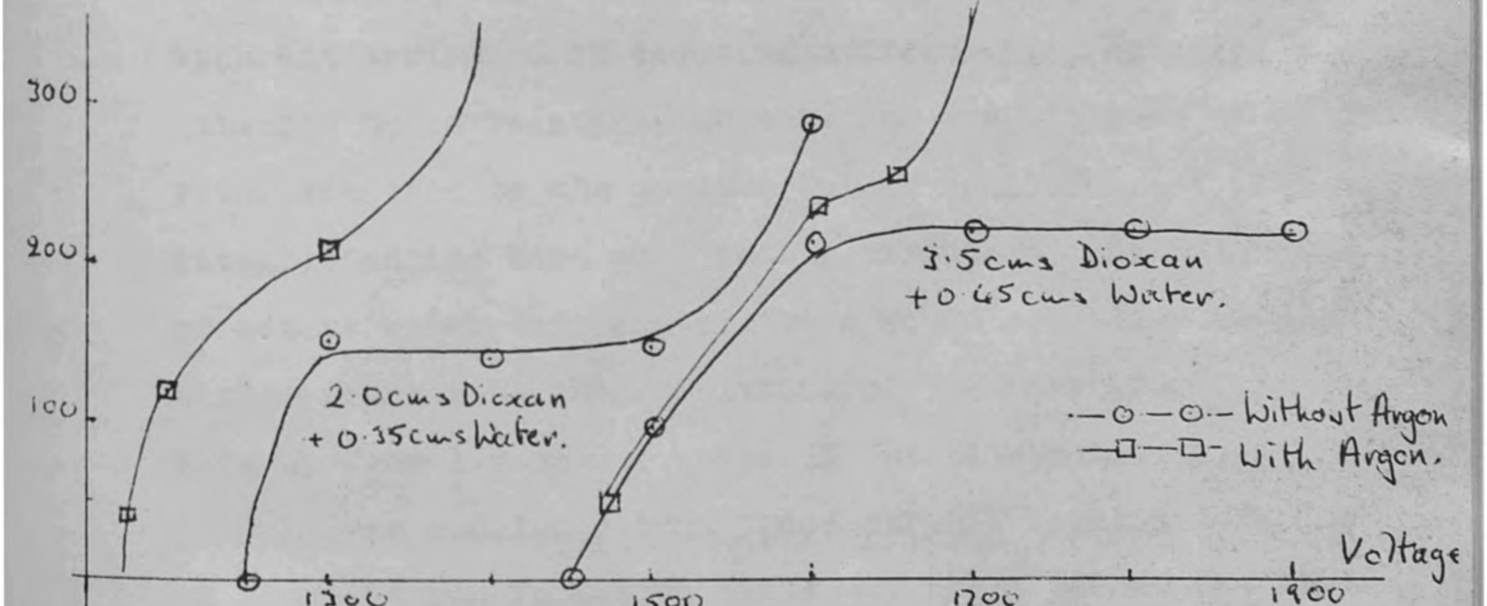


Figure (25). Effect of adding 10 cms pressure Argon to Dioxan-Water fillings.

constituent of the geiger filling was still considered to be essential.

In the absence of argon a very good, stable characteristic was observed,Fig. (24). A curious feature of these fillings is the abrupt fall in count rate at the high voltage end of the plateau just before the counter begins to discharge continuously.

Fig. (25) shows the effect of adding argon to a filling containing various proportions of inactive water and dioxan.

Varying the proportions of water and dioxan,Fig. (26) altered the characteristic of the filling, a noticeable deterioration occurring at low water content. This deterioration was inconvenient because the mixtures of interest in the present work would contain very small proportions of water.

The main objection to this filling was, however, the apparent variation in counting efficiency. Repeated attempts to correlate count rate and the pressure of active water admitted to the counter failed completely. Inconsistencies were such that a mixture to which 1.2 cms of active water had been admitted would sometimes have a higher count rate than a mixture of the same proportions made up from 1.8 cms of water of the same activity.

It was concluded that these erratic results were due to negative ion formation either by the water or the dioxan;

Dioxan Water Fillings

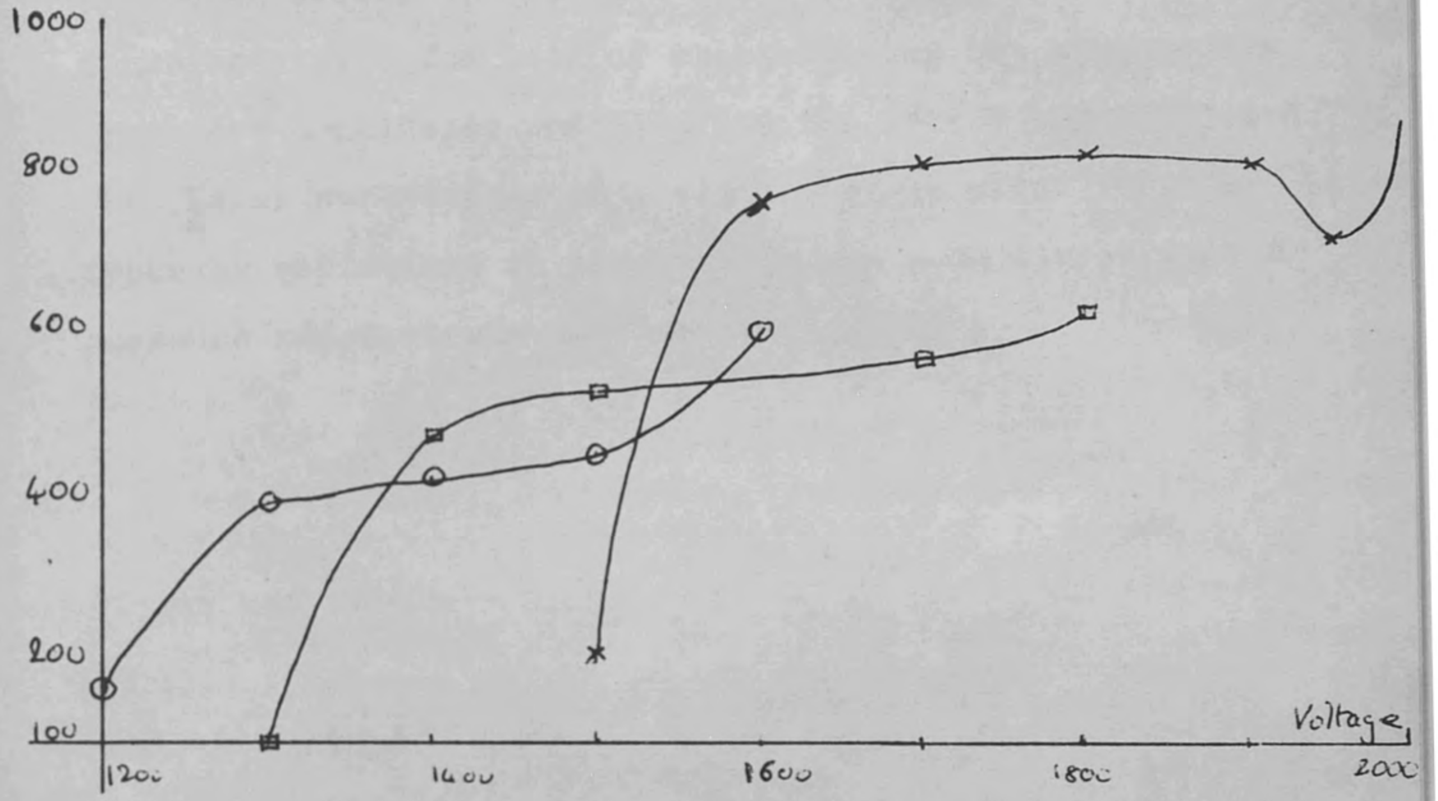


Figure (26). Deterioration of Geiger Characteristic with Decrease in proportion of water vapour.

-×—×- Proportion of Dioxan - Vapour to Water Vapour 2:1

—□—□— 3·3:1

—⊙—⊙— 3·7:1

the counting efficiency would then be expected to vary with the total pressure, and with the partial pressure of both constituents. The task of standardizing the mixture was therefore considered hopeless and the method was abandoned.

Later work suggested a simpler explanation for the apparent variations in sensitivity and some direct vapour pressure measurements were made.

A.

IV.(a)Discussion of Characteristics of Geiger Fillings

Certain features of the characteristics observed in the preceding section are explicable in terms of the current theory of geiger operation.

A brief summary of the theory proposed by Korff and Present in 1944,[32] and amplified by the former author in 1955,[9] is given below.

The many different processes which occur within a geiger tube can be divided into two groups; those which tend to propagate the discharge and those which tend to stop or "quench" it.

A counter will function satisfactorily only if a balance is maintained between these two types of process. In some fillings, such as for example, pure argon, the quenching processes are inadequate and an electronic quenching circuit has to be incorporated in the counting system to prevent the tube going into continuous discharge.

The presence of a polyatomic vapour in the filling gases augments the quenching processes in the discharge and, ideally, renders the external quenching circuit unnecessary. Such fillings are said to be self-quenching, a typical example being a mixture of argon and alcohol in the ratio of 10:1.

The processes initiated by a β-particle in a tube containing argon and alcohol are the following:-

(1) Propagation

(i) A collision between a β-particle and an argon atom or alcohol molecule results in ionization.

(ii) The ions formed by this initial collision are accelerated by the field until the electrons and/or negative ions reach the region of intense field near the central wire anode.

(iii) Under the influence of this field the primary negative particles are strongly accelerated and cause further ionization by collision. In a typical counter tube, operating at about 1000 volts, the field strength at a distance of about a twentieth of a millimetre from the surface of the central wire is about 20,000 volts/cm. The number of new electrons generated by multiple collisions in this region is of the order of 10^8. This amplification process is referred to as the Townsend avalanche.

(iv) The positive ions formed in the avalanche move towards the cathode into the region of low field where the energy acquired between collisions is insufficient to cause ionization. On reaching the cathode neutralization of the argon ions results in the emission of radiation in the wavelengths 1070A to 790A. This is sufficiently energetic to cause ionization in the gas and

(v) the emission of photoelectrons from the surface of the cathode.[11]

(vi) Recombination of ions and the reversion of excited atoms to the ground state also results in photoemission and may lead to photoionization and photoelectrons.

Photons generated in the discharge have been shown by Chawdri et al[37] to be responsible for the onset of the Geiger region. The equal pulses characteristic of the Geiger region being due to the rapid spread of the avalanche, annularly down the length of the central wire.

(2) Quenching

(i) The positive ions generated in the avalanche being, relative to the electrons, very slow moving, form a cyclindrical positively charged sheath round the anode. If the avalanche is sufficiently large, the positive space charge lowers the effective anode voltage and the discharge ceases. The geiger tube is then unable to function until the positive ions have reached the critical radius[38] of the counter. The time required for the positive ions to reach this critical radius is dependent on the size of the ions, the pressure of the filling and the voltage applied to the counter. Under normal operating conditions the dead time of an argon: alcohol counter is about 150 microseconds.

(ii) A high proportion of the radiation emitted by the recombination of argon ions at the cathode is absorbed in exciting the vibrational states of alcohol. The processes of photoionization and photoelectronic emission which would, in the absence of alcohol, result in continuous discharge are therefore, at least partially, prevented.

(iii) The emission of photoelectrons is also prevented by charge transfer between positive argon and alcohol ions. The ionization potential of argon being 15.68 volts and that of ethyl alcohol being 11.3 volts, a collision between a positive argon ion and a neutral alcohol molecule can result in the ionization of the latter and the neutralization of the former. The reverse process is energetically impossible.

Only a fraction of the argon ions originally formed are therefore permitted to reach the cathode.

(b) Discussion of characteristics observed for new fillings

(i) Exclusion of Argon

In the theory of geiger counting there seems to be no fundamental reason for the widespread use of argon in geiger fillings. Furthermore, the presence of argon in the filling is, on the basis of this theory, clearly disadvantageous owing to the energetic radiation emitted when argon ions are neutralised. A proportion of a polyatomic vapour has therefore to be included in an argon filling in order to absorb the radiation which would otherwise ruin the characteristic.

On the other hand there is theoretically no reason to believe that a quenching agent requires the admixture of another component in order to give a satisfactory plateau. The use of argon, in the present research at least, is therefore a needless complication.

The use of helium in the tritium assay technique developed by Bradley and Bush[17] is almost certainly, equally unnecessary. These workers used a helium filling saturated with tritiated acetone. A workable characteristic can be obtained with acetone alone, Fig (27).

Comparison of the properties of the argon-alcohol and alcohol only filling shown in Fig. (10) reveals the higher starting voltage of the latter. Apart from this the main difference is the much more gradual approach both to the geiger region and to breakdown in the alcohol filling. This is in accordance with the theory that the onset of the geiger region and breakdown are due to photons. The fact that ethanol has a geiger region in spite of the fact that it absorbs continuously below 2000A, shows that spread of the discharge must be due either to photons less energetic than those corresponding to 2000A, or to some other process.

(ii) Improvement of Characteristic with Pressure

It is of interest that high pressure methanol fillings were reluctant to breakdown, abnormally long plateaus being observed Fig. (12). The improvement can be explained in terms of a more efficient quenching action. As the pressure is raised, the efficiency of both main quenching processes would be expected to increase. Positive ion quenching improves because the mobility of the ion sheath is decreased, quenching by light absorption improves because the pulse size does not increase proportional with the pressure, i.e. the number of molecules available for absorption of photons is increased by a larger factor than the number of positive ions bombarding the cathode.

McCusker and Rochester[39] observed exactly the opposite effect when the pressure of the alcohol filling is raised, the plateau disappearing altogether when a pressure of 5.5 cms was attained. A possible explanation for these conflicting results is given in a later paragraph.

(iii) Dioxan-Water Fillings

Relative to alcohol, the dioxan-water filling has a much more rapid approach to the geiger region and to breakdown, Fig. (24). This fact together with the ruinous effect of adding argon to the filling, Fig. (25), is readily explained by the transparency of dioxan to the visible and ultra violet light.[44]

The most interesting feature of these characteristics is the "dip" at the high voltage end of the plateau of a dioxan-water mixture shown in Fig. (24). This dip together with the negative slope which preceded it indicate that the filling has an abnormally long dead time. The count rate being 3400 counts per minute, the dead time must be more than 3 milliseconds. The dead time of a counter containing 3 cms of alcohol and 7 cms of argon has been found to be 245 microseconds, this value being fairly typical of fillings in general.

Assuming rough proportionality between the dead time and the size of the positively charged entity, it seems possible that in the dioxan-water mixture, the latter is about 10 times larger than normal. This suggests either that aggregates of dioxan and water molecules exist in the vapour phase or that clustering of the highly polarizable water molecule around ion centres occurs. Although clustering in water vapour has been discussed in other contexts[42] its significance in geiger operation has received little attention.

Alternatively the long dead time may be due to positive ions of normal size moving in a field greatly reduced by an abnormally large space charge. This explanation implies a very high specific ionization constant for the dioxan-water mixture.

The highly abnormal nature of vapour mixture of dioxan and water is strikingly illustrated by the work of Barcarella et al.[45] They found that the second virial coefficient was -7500 mls. The virial coefficient for water is -1163 mls and for dioxan -1690 mls.

(iv) Improvement of Characteristic with Addition of Water Vapour

It has been repeatedly noticed that the addition of water to an alcohol filling improves the characteristic Fig. (15). Although the abnormal dip at the end of the dioxan-water plateau was never observed in aqueous alcoholic fillings, it seems possible that ion clustering also occurs in these. Ion clustering would result in the formation of large positively charged entities of low mobility and therefore a longer dead time and a flatter plateau. A longer dead time would also result in a slight decrease in efficiency and this has been observed.

This would account for the poorer characteristic observed when alcohol is dried before use and also for the divergence mentioned between the result obtained in this work and those obtained by McCusker and Rochester. McCusker and Rochester used absolute alcohol whereas the alcohol used in the corresponding experiment in this work had been distilled but not dried.

The stability of ion clusters has been investigated by Livingstone.[43] He calculated the equilibrium pressures of hydrogen bromide centred on bromine ions and found, for the first layer a pressure of 10^{-3} mms and for the second, several atmospheres.

If the corresponding pressures for water vapour are assumed to be of the same order of magnitude, it is clear that the size of the cluster (if they occur) will not vary significantly with the limited variations in the partial pressure of water which is practicable in normal geiger operation.

In rigorously dry conditions clustering could not occur. The erratic characteristics reported by Anderson[31] who worked at pressures of 10^{-6} mms are of interest in this connection.

The dead time of slightly aqueous methanolic fillings has been measured and found to be 500 useconds. This is higher than the dead time usually reported for geiger fillings and supports the suggestion that ion clustering may be an important factor in geiger operation.

(v) Characteristics with Negative Slope

The fall in count rate with increasing voltage which is sometimes observed in alcohol fillings has been shown to be due to the condensation of tritiated vapour (Section A III (v)). Similar characteristics have also been reported by Jackson and Lampe[36] but the simple explanation given above cannot apply to their filling because it contained no tritium in the vapour phase. Their results can, however, be explained in terms of the fundamental discharge processes within the tube. Negative current-voltage characteristics are, in fact, by no means uncommon in low pressure discharges between coaxial electrodes. A recent paper by Jatar[40] summarizes current explanations of this effect and concludes in favour of the space charge theory of Druyvesteyn and Penning.[41] Their theory is the basis of space charge quenching outlined in Section A IV (a) and applied to explain the "dip" in the dioxan-water characteristic in Section A IV (b) (iii).

(vi) Summary of Results on New Assay Methods

(1) Ethanol, Methanol and aqueous dioxan vapours, in the absence of argon, have good counting properties.

(2) Water vapour alone has very bad counting properties which improve very suddenly on warming the counter tube.

(3) The count rate varies linearly with tritium content, and with the pressure of the filling for both methanol and ethanol. These vapours are therefore suitable for tritium assay.

(4) Water vapour up to about 25% of total pressure was found to improve the characteristic of alcohol fillings and to decrease slightly their counting efficiency.

(5) Air spoils the characteristic of alcohol fillings and increases the counting efficiency. Neither effect is significant until the air pressure reaches about 5% of the total.

A.

V. Final Assay Procedure

Methanol rather than ethanol was chosen as the counting gas because of its higher vapour pressure and lower starting voltage.

The methanol was distilled, but not dried, before use.

The vacuum line required was similar to that shown in Fig. (2) except that the bulb A was no longer needed. p15

The sample to be analysed was attached at one of the joints behind T_6 or T_7 and degassed once. Prior to filling, the geiger tube, attached at T_{gm}, was evacuated to less than .01 mm pressure. Taps T_{gm} and T_4 were then closed and the manometric chamber flushed with the sample vapour. After this had been pumped away, T_4 was closed again, T_{gm} opened and the sample admitted into the counter, until a pressure of between 5 and 8 cms had been attained. T_{gm} was then closed and the tube detached and placed in the lead castle which was maintained at a temperature of about 32°C. The general shape of the characteristic was then determined by taking quarter minute counts over the entire voltage range. This preliminary count enabled the rejection of unsatisfactory fillings without further loss of time.

After about 10 minutes the position of the plateau which moved towards higher voltages on heating was found again by taking quarter minute counts. It was important at this stage to avoid exceeding the breakdown voltage, because the characteristic of the filling would be altered if a continuous discharge were allowed to occur.

Three voltages were then selected, one near each end of the plateau and one in the middle, and the final counts determined at these points. The counting time was adjusted so that the sum of these three counts was about 10,000.

The statistical error was therefore about 1%.

The average count rate of the sample was found either graphically or by dividing the total number of counts by three.

The count rate thus obtained had to be corrected for dead time, background count, counter efficiency, room temperature during filling and pressure of methanol in the filling, Table II.

B. VAPOUR PRESSURE MEASUREMENT

I. PRELIMINARY

(i) MEASUREMENT OF VAPOUR PRESSURES USING RADIOACTIVE ISOTOPES

Radioactive isotopes have not so far been very extensively used for the measurement of low vapour pressures. Such measurements which have been reported have been mainly concerned with the vapour pressure of metals, e.g. zinc[46,47] and silver.[48]

Dainton and Kimberley[49] measured the vapour pressure of white phosphorus over a range of temperatures using a static apparatus with an end window Geiger-Müller tube aligned with the vapour space.

Tracer techniques are potentially most useful in the measurement of small partial pressures. This is partly because sensitive techniques have already been developed for the measurement of very small vapour pressures of pure substances and partly because partial pressures are, in general, of greater theoretical interest in that thermodynamic functionsof mixing can be derived from them.

(ii) DIOXAN-WATER SOLUTIONS

The simple assay method developed during the first part of this research enables the partial pressures of water in very weakly aqueous solvents to be conveniently measured. Aqueous dioxan was chosen for the present investigation because there is evidence of abnormally strong interaction between the two components, not only in the liquid phase but in the vapour phase also. Thus Coates and Sullivan[58] concluded from the heat of mixing and from the freezing point curve, that hydrogen bonded complexes occur between six molecules of water and one of dioxan.

Barcarella et al.[45] measured the virial coefficient of dioxan:water mixtures and found it to have the very high value of -7511 mls., much higher than that of either pure component. This implies that water is more strongly hydrogen bonded to dioxan than it is to itself.

Hovorka[54] measured the partial pressures of dioxan water solutions and found that in solutions of high water content, the partial pressure of water was higher than that of pure water.

Pressure measurements in this system are also of interest because aqueous dioxan is a useful solvent in some physical chemical experiments. The interpretation of results, for example in kinetic work, requires a knowledge of the activity coefficients of the components of the solvent.

(iii) METHOD OF MEASUREMENT OF VAPOUR PRESSURE

A static method was adopted, i.e. a known volume of vapour in equilibrium above the solution was condensed and assayed for tritium.

The mole fraction of water in the solution studied ranged from .004 to .09, and the partial pressures from 0.3 mm of Hg to 10 mm of Hg.

Strictly speaking, the partial pressures obtained in this way are those of partially tritiated water (THO) in solution with a very large excess of ordinary water and dioxan.

The actual partial pressures measured, i.e. the partial pressure of THO, are in the region of 10^{-5} to 10^{-6} mm, and correspond to THO mole fractions of 10^{-9} to 10^{-8}.

Expression of the results in terms of partial pressure of water is valid if mixtures of water and tritiated water are ideal.

B.

II. EXPERIMENTAL

(i) SOLUTIONS

Dioxan: The dioxan was purified by refluxing with hydrochloric acid under nitrogen, removing the hydrochloric acid with sodium hydroxide pellets, distilling and drying over calcium chloride and then over sodium. Fresh sodium was pressed into the dioxan periodically. About 100 mls of the purified dioxan was kept under vacuum in a storage bulb D on the vacuum line, Fig. (28). This part of the vacuum line, which was reserved for making up solutions, was silicone treated.

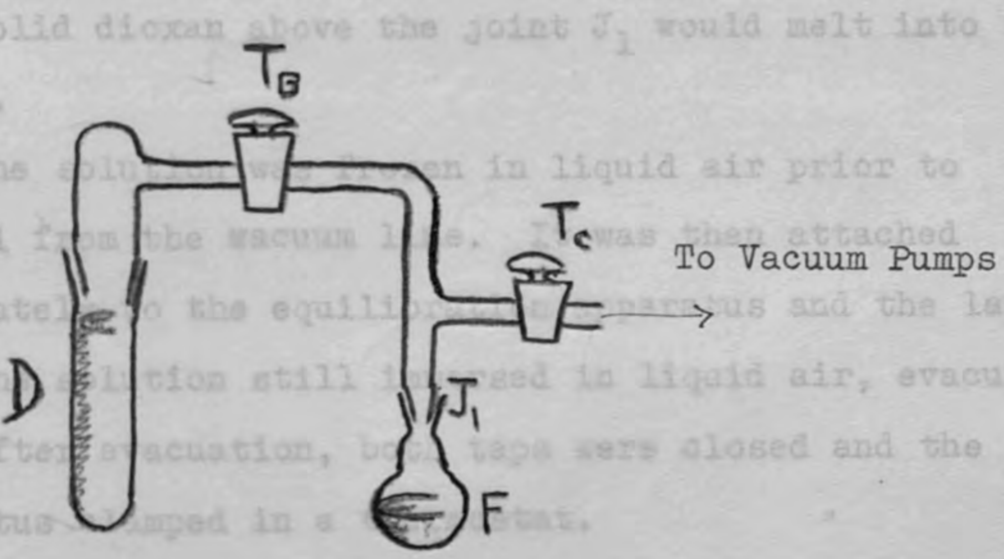


Fig. (28)

Preparation of Solutions

Tritiated water was introduced into a weighed 25 ml silicone treated flask from a fine dropper. The flask was stoppered immediately and weighed.

The flask F was then attached to the vacuum line, the water frozen in liquid air and the space bounded by the flask and taps T_B and T_c evacuated. T_c was then closed and the water allowed to warm up in order to degass. Degassing was repeated twice, after which the water was frozen again in liquid air, the tap T_c remaining closed, and the dioxan allowed to distill in by opening T_B. After the required quantity of dioxan, estimated from the decrease in volume in the storage bulb, had been distilled over, tap T_B was closed and the solution allowed to warm up ~~to~~ so that solid dioxan above the joint J_1 would melt into the vessel.

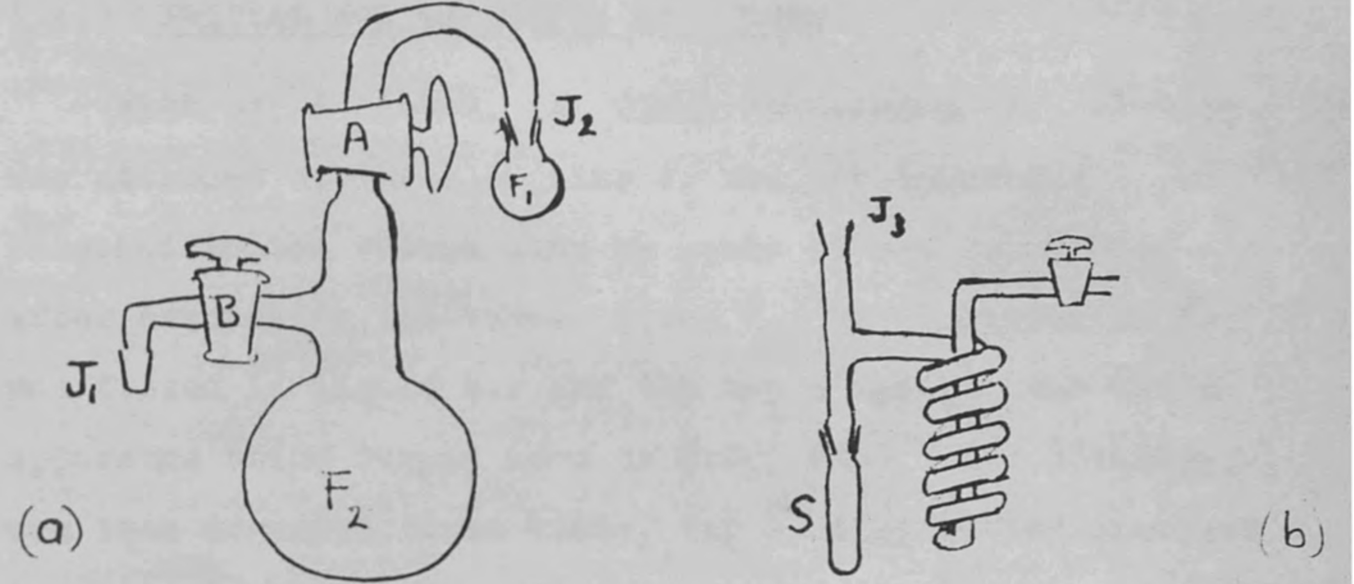
The solution was frozen in liquid air prior to removal from the vacuum line. It was then attached immediately to the equilibration apparatus and the latter, with the solution still immersed in liquid air, evacuated.

After evacuation, both taps were closed and the apparatus clamped in a thermostat.

(ii) APPARATUS USED FOR EQUILIBRATION

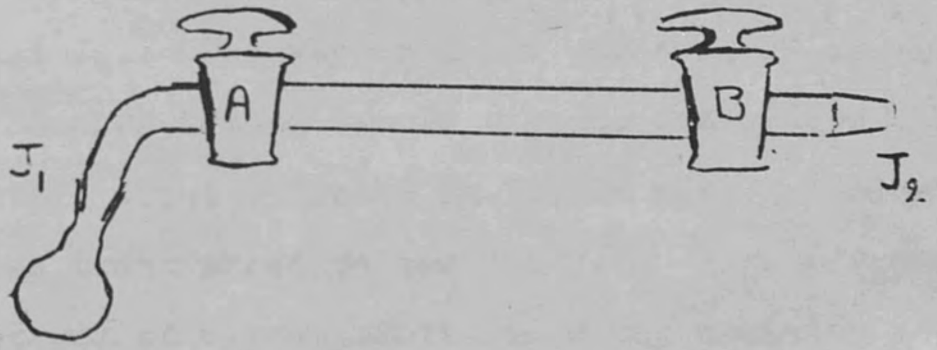
The equilibration vessel used in the first series of measurements was of the type shown in Fig. (30a). F_1 was a 20 ml flask containing the mixture of dioxan and water, F_2 a flask of about 300 ml volume. The volume of the space enclosed by the taps A and B was determined by weighing when full of water. The tap A was of 10 mm bore and the tap B, 6 mm.

Figure (30)



(a). Static Equilibration Apparatus. Type I

(b) Vapour Trap and Sample Tube



(c) Static Equilibration Apparatus Type II

(iii) INITIAL EQUILIBRATION PROCEDURE

With tap A closed, the flask containing the solution was attached at the B14 joint J_1 and the apparatus attached to the vacuum line by means of the joint J_2. After evacuating the vapour space F_2, the solution in F_1 was frozen in liquid air and the tap A opened, the whole apparatus being pumped down to 0.005 mms. The solution was then degassed three times, tap A being closed whenever the solution was being allowed to warm up to room temperature.

After a final evacuation to approximately one micron, both taps were closed and the apparatus removed from the line and clamped in a thermostat. A period of three quarters of an hour was allowed to enable the apparatus to attain the required temperature and equilibration was then started by opening tap A.

After equilibration tap A was closed and the apparatus reconnected to the vacuum line, Fig. (30b), through the joints J_2 and J_3. The vapour phase was trapped in the spiral and then condensed into a sample tube S, containing a known volume of ethyl alcohol frozen in liquid air. The sample tube was then transferred to the joint S_2, Fig. (2), and a certain pressure of vapour admitted to the counting tube. At this stage the 10:1 argon:alcohol filling was still in use and the procedure described in Section A II (iii) was followed.

The results obtained in this way were extremely erratic and bore no relation to the partial pressure values obtained by other workers. In general the results were too high by a factor of 2 to 6.

A possible explanation of this was multilayer adsorption of water on the walls of the vessel. Accordingly the apparatus was treated with a solution of dichlorodimethyl silane in carbon tetrachloride and the silane polymerized with steam.

No improvement was observed. However, the silicone treatment was considered to be a useful precaution, and all equilibration apparatus used in subsequent work was treated in this way before use.

A second possible explanation of high results was condensation of vapour on regions of the apparatus with a small radius of concave curvature. The equilibrium vapour pressure of a liquid in a concave layer being slightly lower than that on a plane surface, high results would be expected if concavities were present in the vapour space of the apparatus.

Several modifications of the apparatus in Fig. (30a) were made, irregular joints in glass blowing being carefully avoided.

Equally erratic results were obtained with modified apparatus. For a time suspicion fell upon the assay technique and this was reinvestigated. It was at this point that the argon component of the Geiger filling was found to be unnecessary. The subsequent work on the alcohol filling established the improbability of future assay errors exceeding a few per cent and permitted the unsuccessful equilibrations to be detected with a minimum waste of time and argon.

Eventually it was found that a small temperature differential between the liquid phase and the vapour phase reduced the tritiated water content of the vapour phase to approximately the right value.

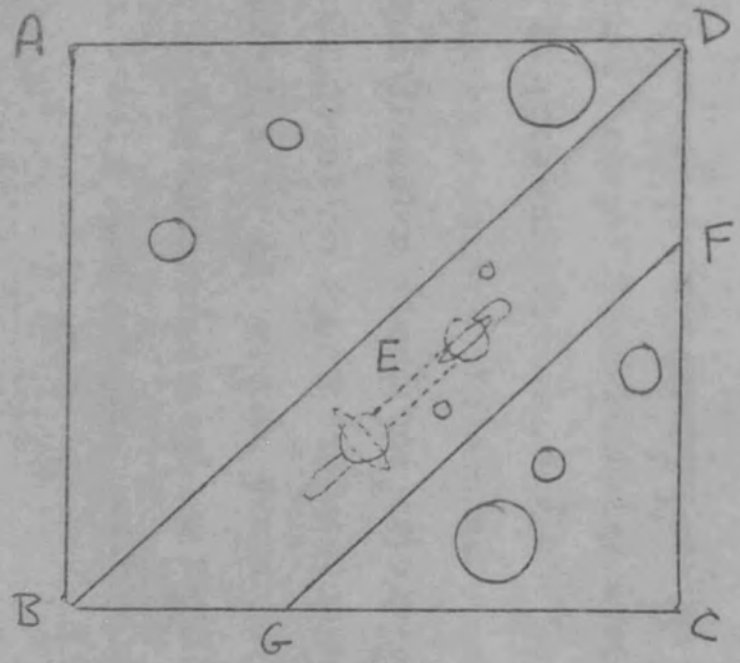
It was concluded that condensation in the vapour space was the cause of the high results. In an apparatus, all parts of which are at the same temperature, there is no fundamental reason why a liquid phase should exist in one part of the apparatus and not in another.

A temperature differential of about 1.5°C was therefore adopted during all subsequent equilibrations, the slight inaccuracy thereby introduced being, apparently unavoidable.

Hansen and Miller[50] also found that a temperature differential was essential in their work on aqueous alcohol solutions.

(iv) APPARATUS REQUIRED FOR MAINTENANCE OF A TEMPERATURE DIFFERENTIAL

The maintenance of a controlled temperature difference



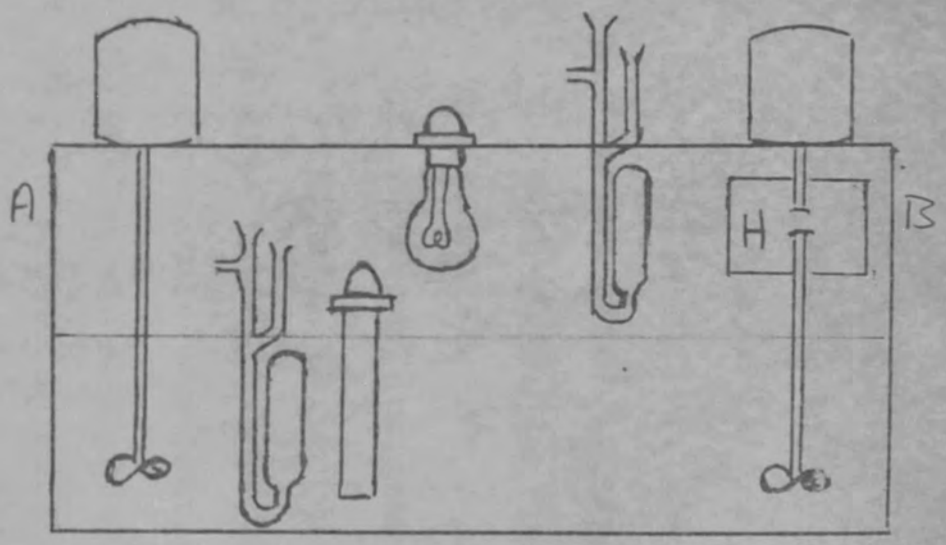
BD Glass Partition

BDFG Asbestos Lid

CFG Metal Lid Supporting
Motor, Regulator & Lamp

E Equlibration Apparatus

H Cardboard Blade



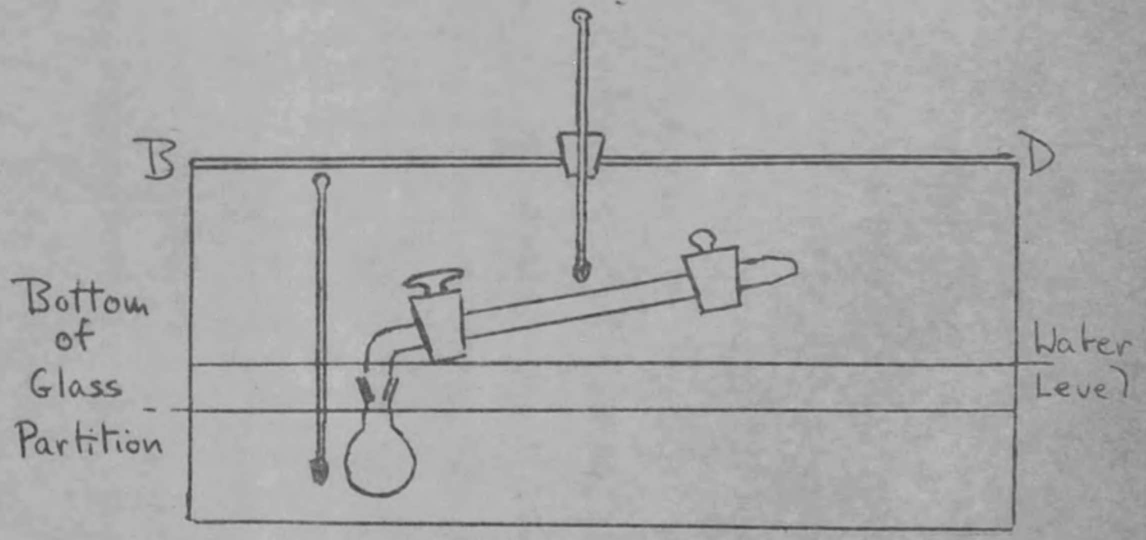


Figure (51)

between two parts of the same apparatus presented practical difficulties. The problem was solved, moderately successfully by half filling a large thermostat with water, enclosing part of the air space above it, and thermostating both the water and the air in the enclosure with conventional thermoregulating equipment. The air in the enclosure was circulated by a cardboard blade threaded onto the shaft of the motor, mounted on top of the enclosure, which stirred the water. A 40 watt bulb was found to be an adequate heating element for the air chamber. Control of the water temperature was better than ± 0.05°C, but the air temperature control was much less reliable, variations of approximately 0.5°C occurring during half hour periods.

The construction of the thermostats is illustrated in the Fig. (31).

Having finally succeeded in obtaining meaningful vapour pressure measurements it was possible to undertake three essential preliminary studies before returning to the main problem of measuring the partial pressure of water in aqueous dioxan. It was necessary to investigate the equilibration time, the effect of the size of the equilibration apparatus on the measurements, and the possibility of tritium exchange between water and dioxan.

The apparatus used in this work was a small one of extremely simple (and possibly novel) design which had been adopted for reasons of speed and convenience during the period when abnormally high results were being obtained.

It consisted simply of a straight tube with two 8 mm bore taps and B 19 joints at each end Fig. (30c). To one of the joints the flask containing the solution was attached. The volume of the vapour space was 31.6 mls. After equilibration the apparatus was attached to the vacuum line and the vapour phase analysed, by a procedure to be described in detail in a later section.

(v) DETERMINATION OF TIME REQUIRED FOR EQUILIBRATION

Table III gives the count rate observed after different equilibration times. These figures do not alter significantly for equilibration times greater than 15 minutes.

Sample	Time of Equilibration Minutes	Count Rate
1.	5	950
	15	1493
	60	1485
2.	140	1157
	220	1205
	300	1160

Table III

This result was confirmed by the following experiment. About 2 mls of an aqueous dioxan solution containing tritiated water was frozen into a Geiger tube which had been previously evacuated. The tube was removed from the vacuum line and placed in an unheated lead castle. Room temperature was 24°C.

As the tube warmed up the contents melted and evaporated. The latter process was followed by measuring the count rate every ten minutes.

The count rate at a voltage of 1700 is shown below:

Time Minutes	Count Rate
10	686
20	842
30	849
40	822
50	870
60	849

Table IV

It was concluded that equilibration times longer than 20 minutes would be adequate. For most subsequent measurements equilibration times of between 30 and 60 minutes were adopted.

(vi) WALL EFFECT

As static vapour pressure apparatus conventionally used is usually several litres in volume, it was feared that the small apparatus, having a large internal surface/volume ratio in the vapour space, would be disadvantageous for the measurement of vapour pressures.

Accordingly an even smaller apparatus having a volume of 9.3 mls and therefore a higher surface volume ratio was constructed and the results from the same solution under the same conditions compared, it being expected that adsorption on the wall would give a higher value for the small apparatus.

As both apparatus gave results which agreed within the experimental error, there seemed to be no reason to believe that erroneous measurements would result from the reduction in size. The advantages of the small apparatus in work of this kind are of considerable importance.

Firstly, if the vapour space is small, only a relatively small quantity of solution need be used. The weight of solution required is governed by the change of mole fraction during equilibration. This change should be negligible and consequently, the weight of solution must be large or the volume of the vapour space small. The latter condition is more convenient and more economical, but it can be adopted only when a sensitive analytical method, such as the present one, is practicable.

A further advantage of small equilibration vessels is the minimization of the error arising from adsorbed water. This error could be surprisingly large, as the following calculation (based on Bent's and Lesnick's[33] figures for residual adsorbed water on glass apparatus) shows.

After two hours evacuation at 10^{-3} mm, an apparatus of internal surface area 400 sq. cms would retain about 0.8 mg of water. If 10 gms of a solution containing .005 mole-fraction water (ca. 10 mg.) were equilibrated in an apparatus of this size an error of about 8% in the composition of the solution would result.

If solutions of lower water content are to be investigated it is clearly essential either to increase the amount of solution, or to decrease the size of the apparatus.

This error cannot be eliminated by heating the apparatus under vacuum. Bent and Lesnick found that 2 hours heating at 304° C under a vacuum of 10^{-3} mms reduced the amount of adsorbed water, but only by a factor of two.

It is probably that the silicone treated equilibration apparatus used in this work would retain considerably less water.

However, even if the effect of silicone is neglected, the apparatus and the weight of solution used were small enough and large enough respectively to reduce the composition error to less than 0.5%. This figure applies to the weakest solution studied i.e. to a solution of .004 mole fraction water.

The error for solutions of higher water content will, of course, be less.

(vii) EXCHANGE OF TRITIUM ATOMS BETWEEN WATER AND DIOXAN

A third problem which had to be investigated before vapour pressure measurements of the kind proposed could be considered valid was the possibility of exchange occurring in the solutions prior to and during equilibration.

Although it was initially thought to be unlikely that the carbon bonded hydrogens of dioxan would undergo exchange Wilzbach[8] had recently shown that the apparently equally improbable exchange between gaseous tritium and aromatic compounds did occur.

The possibility of exchange was tested by performing two equilibrations with the same dioxan-water solution, one a fortnight after the other. The vapour phase was condensed in liquid air and assayed for tritium using the procedure described in the next section.

The results given in Table V~~I~~ agreed to within the statistical assay error of the experiment and show that exchange during this time interval is negligible.

	Date	Count Rate
Table V	6th November	1977
	22nd November	2012

(viii) PROCEDURE FOR ANALYSIS OF VAPOUR PHASE

After equilibration the whole apparatus is removed from the thermostat and attached to the vacuum line at joint J_E Fig. (32). The methanol in the sample tube S is frozen in liquid air and the intervening parts of the apparatus evacuated to a pressure of 0.005 mm. Tap T_9 is then closed and taps T_7 and T_{11} opened so that the whole of the vapour phase in E condenses in the sample tube. Trapping out was normally complete in a few seconds but as a precaution against a leak during the equilibration the time allowed for trapping was five minutes. After trapping, Tap T_9 is opened and the residual pressure measured on the manometer. Ideally this should be zero, indicating that no leakage had occurred throughout the experiment. If a measurable depression was observed, the sample was rejected, for this meant that either equilibration or trapping was incomplete.

The sample tube was then isolated by closing tap T_7, the liquid phase in the vapour pressure apparatus was frozen down in liquid air and the whole apparatus evacuated

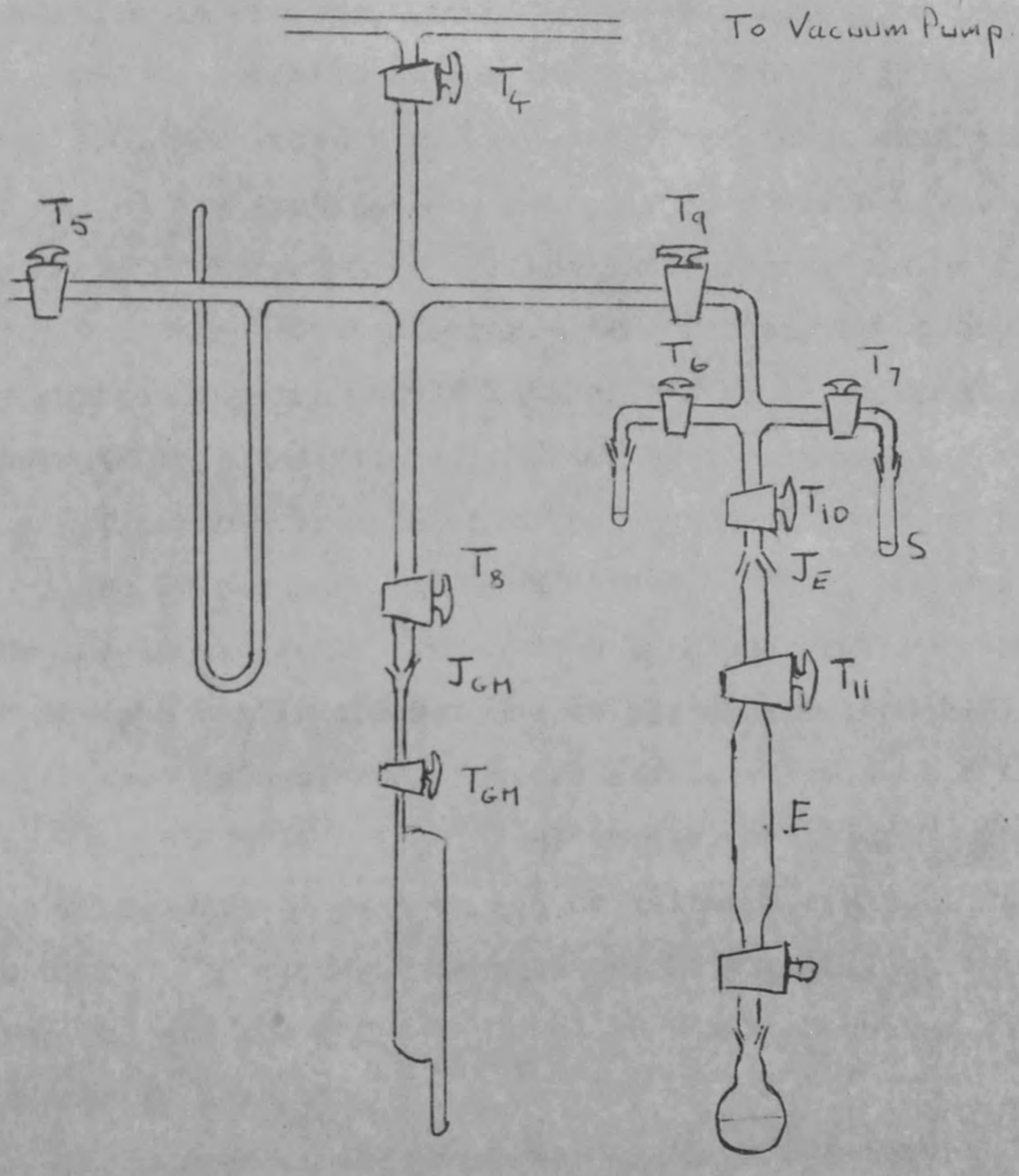


Figure (32)

to 0.005 mms prior to detachment from the vacuum line and immersion in the thermostat for another equilibration.

Before introducing the contents of the sample tube into a Geiger tube it was necessary to ensure completeness of mixing and exchange and secondly to guard against exchange of hydroxyl groups while the vapour was on its way from the tube to the counter. The former was accomplished by surrounding the sample tube with warm water until the contents refluxed, and the latter by flushing the manometric chamber once with the vapour and pumping away.

The Geiger tube was then attached at J_{gm} and evacuated, the sample was again frozen down in liquid air and the whole of the manometric chamber evacuated to less than 0.01 mm. Tap T_7 was then closed, and the sample allowed to attain room temperature. Tap T_4 was then closed, tap T_7 opened and a pressure of ca 5 cm - 8 cm methanol admitted to the counter. The time and temperature of the filling were recorded and the counter placed in the warmed lead castle as soon as possible.

A quarter minute count was taken immediately to ascertain the approximate plateau characteristics and count rate, partly in order to ensure that time is not wasted if the filling should prove to be unsatisfactory and partly so that an approximate result is available if before the accurate count some calamity such as a leak should befall

Calculation of Partial Vapour Pressure of Water

Specimen Table of Experimental Data

Mole Fraction Water in Dioxan 0.033 Temperature of Equilibration 18.00 ± 0.05°C

Sample No.	Time of Equ^n Mins	Volume of MeOH in Trap mls	Geger Müller Tube	Temp. of Filling °C	Temp. of Lead Castle °C	Pressure of Sample in G.M. Tube Cms Hg	Obs^d Count Rate	Counts per Minute								Weight of H_2O in Vapour μgms	Partial Pressure H_2O mms Hg.
								Corrections for :-									
								Dead Time	Back Ground	G.M. Tube Efficiency	% Mean Deviat^n	Average Count.	Vol. of MeOH in Trap	Pressure to 5.0 Cms Hg	Temp. to 0°C		
1	95	0.5	NE 1808	20	33	5.0	1667	1908	1846	1900	3.1	1843	1843	1843	1977	38.45	4.18
			MF 925				1798	1838	1785	1785							
2	150	0.5	NE 1808	18	33	5.05	1814	1855	1791	1841	3.1	1786	1786	1771	1890	36.90	3.91
			MF 925				1753	1794	1731	1731							
3	60	0.5	NE 1808	19	33	5.0	1832	1873	1802	1851	1.3	1875	1875	1875	1981	38.52	4.19
			PH 1113				1928	1969	1899	1899							
4	48	0.5	NE 1808	14	30	5.2	1930	1970	1902	1960	1.5	1991	1991	1917	2012	39.02	4.24
			MF 925				1985	2025	1960	2019							

Table II

the counter and render the filling useless. After the counter had been in the lead castle for fifteen minutes, the activity of the filling was accurately measured.

(ix) CALCULATION OF PARTIAL PRESSURES FROM OBSERVED COUNT RATE

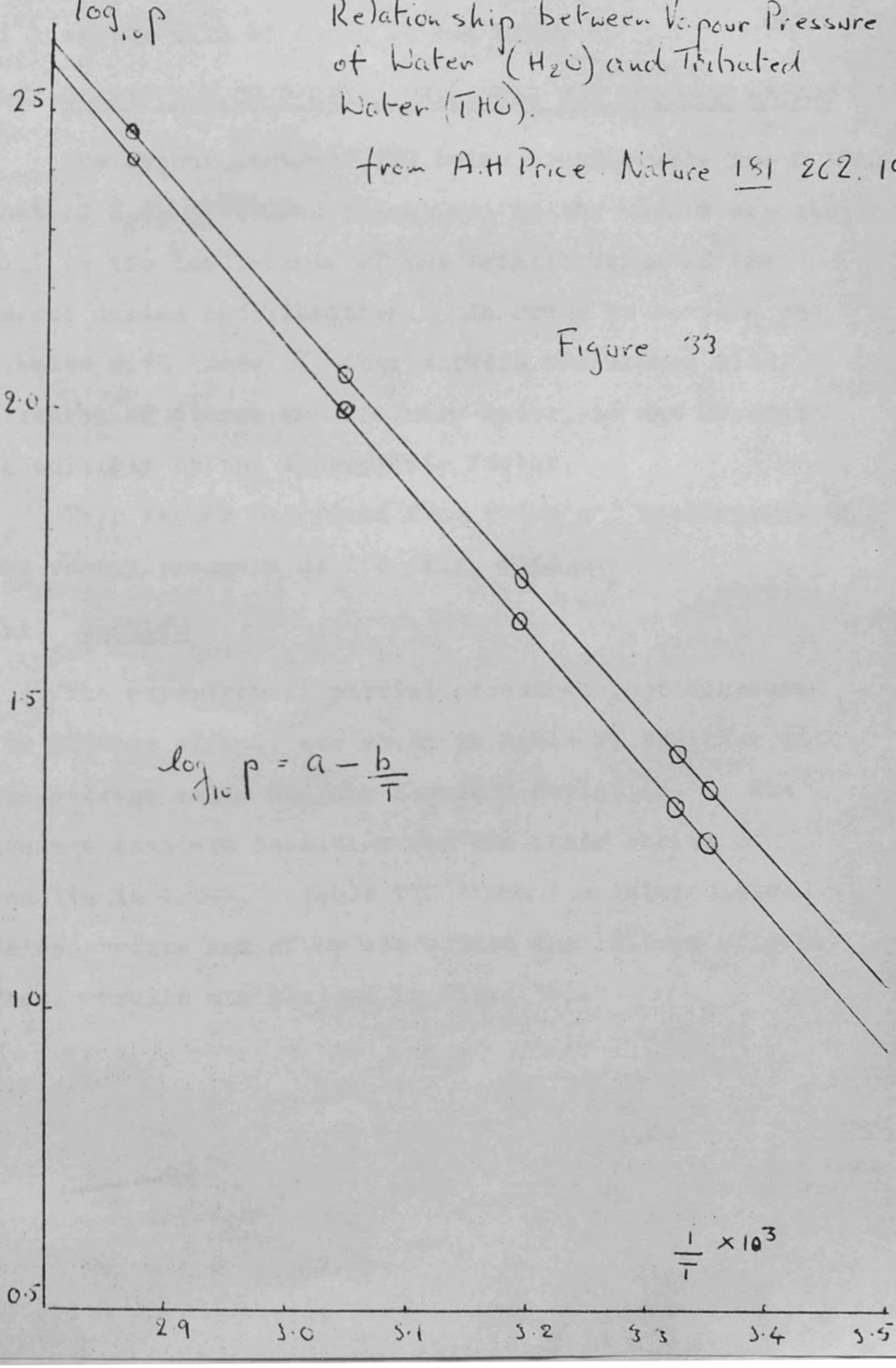
The stages in this calculation are illustrated by Table II. The weight of water in the vapour phase is calculated from the ratio between the corrected count rate and that of the standard solution Fig. (14).

In the absence of comprehensive data on the second virial coefficient of vapour mixtures of dioxan and water ideality had to be assumed in calculating the partial pressure of water.

The only experimentally determined virial coefficient for dioxan:water is due to Barcarella et al., and applies to mixtures containing 50% to 70% dioxan. It has an abnormally high value (-7511 ml see page 47) which suggests that molecular association occurs in the vapour phase.

There is considerable additional evidence[52] in favour of polymerization in the vapour phase especially for those substances, such as the alcohols, which are capable of forming hydrogen bonds.

If the virial coefficient in the vapour concentration studied in this work is of the same order as that found by



Relationship between Vapour Pressure of Water (H_2O) and Tritiated Water (THO).

from A.H Price. Nature 181 262. 1958

Figure 33

Barcarella, partial pressures calculated on the assumption of ideality will be about 2% too high.

(x) CORRECTION OF PARTIAL PRESSURES FOR ISOTOPE EFFECT

The vapour pressure of THO being considerably lower than that of H_2O, pressures calculated in the manner described will be too low because of the fractionation of the vapour during equilibration. In order to compare the results with those of other workers who worked with mixtures of dioxan and ordinary water, it was necessary to multiply by the appropriate factor.

This factor was found from Price's[51] measurement of the vapour pressure of THO Fig. (33).

(xi) RESULTS

The experimental partial pressures (not corrected for isotope effect) are shown in Table VI together with the average value and the standard deviation. The average standard deviation for the whole series of results is 4.84%. Table VII shows the interpolated values before and after correction for isotope effect. These results are plotted in Fig. (34).

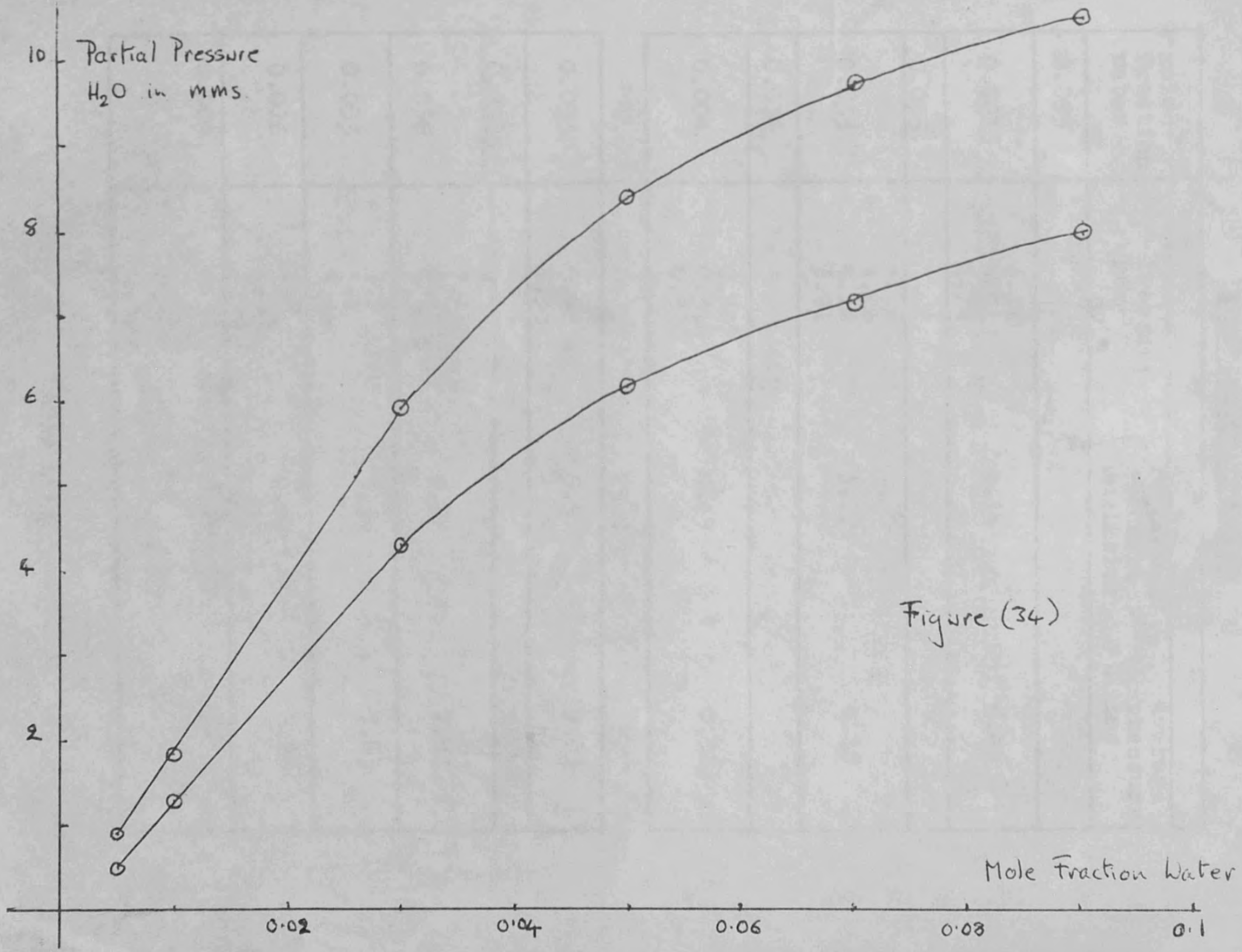

10
8
6
4
2
Partial Pressure
H_2O in mms
0·02
0·04
0·06
0·08
0·1
Mole Fraction Water

Figure (34)

PARTIAL VAPOUR PRESSURE MEASUREMENTS

EXPERIMENTAL RESULTS

mole fraction water	Pressure mms	Percentage standard deviation	Average pressure mms
		18°C	
0.093			
0.0815	6.11 6.41 6.76	4.14	6.43
0.056			
0.033	4.18 4.24 4.18 3.91	3.27	4.13
0.016			
0.004	0.307 0.310 0.310	0.45	0.309
		25°C	
0.093	9.48 8.55	5.5	9.03
0.0815			
0.056	8.1 7.45 8.45 7.26	6.2	7.81
0.033	5.2 5.8 5.88	5.36	5.63
0.016	2.7 2.57 2.92	5.44	2.73
0.004	0.495 0.476 0.507 0.500	2.29	0.494

Table (VI)

Table (VII)

PARTIAL VAPOUR PRESSURE MEASUREMENTS

INTERPOLATED AND CORRECTED VALUES

mole fraction water	Pressure H_2O mms 18°C	Pressure H_2O mms 25°C	Pressure THO mms 18°C	Pressure THO mms 25°C
0.090		9.0		10.5
0.070	5.86	8.32	7.15	9.75
0.050	5.0	7.20	6.2	8.42
0.030	3.55	5.07	4.33	5.96
0.010	1.075	1.57	1.31	1.86
0.005	0.425	0.775	0.518	0.91

B.

III. DISCUSSION OF RESULTS OF PARTIAL PRESSURE MEASUREMENTS

(i) COMPARISON WITH PUBLISHED WORK

Partial pressures of the system dioxan-water have been measured at 25°C by Hovorka et al.[54], and Vierk.[53] Agreement between their values for water is not very good particularly for solutions weak in dioxan.

mole fraction	partial pressure of water mms.	
water	Hovorka	Vierk
0.1	10.2	10.9
0.5	19.1	17.0
0.9	25.9	21.0

Both sets of results include only one point in the concentration range studied in the present investigation. Agreement between the pressure measurements obtained in this work and interpolated values for Hovorka's and Vierk's results is good for solutions containing 0.09 mole fraction water but poor for 0.05 mole fraction water.

mole fraction	partial pressure of water mms		
water	Hovorka	Vierk	This Work
0.05	7.3*	6.6	8.4
0.09	9.9	10.4	10.5

* Estimated from a small graph in original paper.

Partial pressures of water at 18°C in this system do not appear to have been measured by any other workers.

(ii) RELATIONSHIP BETWEEN ACTIVITY COEFFICIENT AND CONCENTRATION OF WATER

Figure (35) shows the relationship between the logarithm of the activity coefficients derived from these pressure measurements and the square of the mole fractions of the components of the mixture. The relationship is linear at both temperatures over the range 0.02 to 0.09 mole fraction of water. The pressure measurements in this range can therefore be considered to be reliable.

At lower concentrations of water, the relationship changes abruptly. Although it is not improbable that the nature of an aqueous solution should change markedly as the water content is reduced to a very low value, the pressure measurements in this range can be accepted with less confidence.

Activity Coefficients

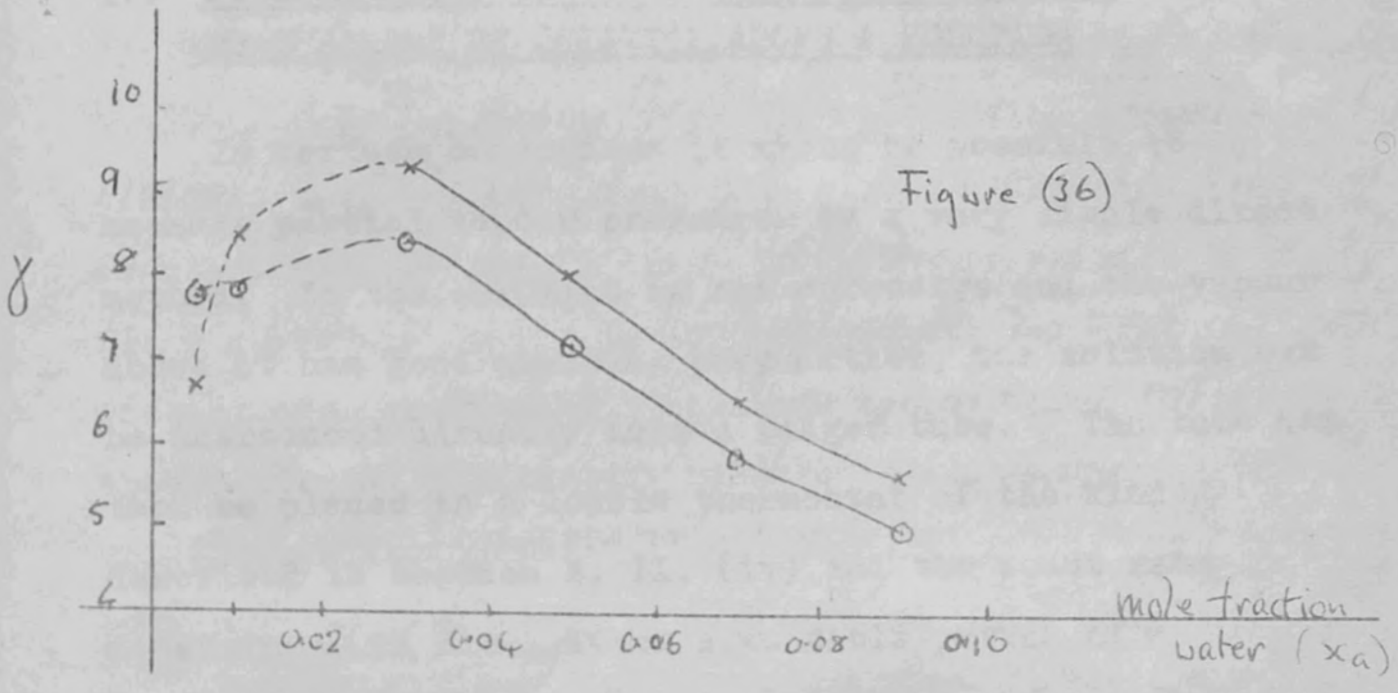


Figure (36)

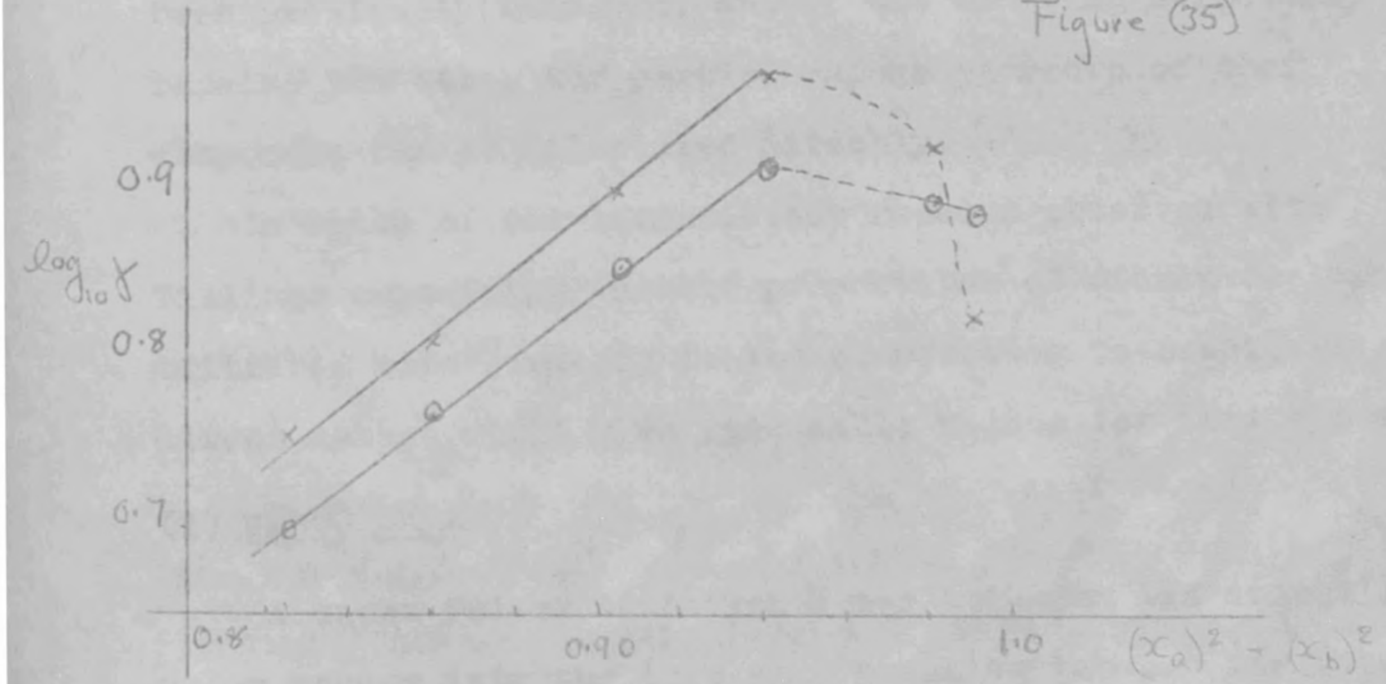


Figure (35)

B.

IV. DETERMINATION OF VAPOUR PRESSURE BY DIRECT MEASUREMENT OF ACTIVITY ABOVE A SOLUTION

In certain conditions it might be possible to measure partial vapour pressures by a very simple direct method. If the solution is not corrosive and the vapour above it has good counting properties, the solution can be introduced directly into a Geiger tube. The tube can then be placed in a double thermostat of the kind described in Section B. II. (iv) and the count rate determined, in situ, after a suitable period of equilibration.

If the count rate of a filling containing a known pressure of the vapour of the radioactive component has been previously measured, and if the counting efficiency remains the same, the partial vapour pressure of that component can be calculated directly.

In spite of the inconsistent results observed with fillings containing various proportions of dioxan vapour and tritiated water vapour, it was interesting to see if this direct method would give reasonable values for this system.

(i) PROCEDURE

A known volume of dioxan water solution was distilled under vacuum into the trap of a counting tube. The tube was then clamped in a thermostat and the count rate determined after forty minutes. Count rates were determined for solutions of 0.1045 and 0.615 mole fraction water at temperatures of 18°C and 25°C. A temperature gradient of 1.5°C was maintained. The count rate was also measured at intermediate temperatures using a dewar flask containing water at the appropriate temperature instead of a thermostat. At these temperatures the air thermostat was unnecessary because the laboratory temperature was normally 21°C - 23°C.

(ii) CALCULATION OF PARTIAL VAPOUR PRESSURE FROM COUNT RATE

As early attempts to standardize the dioxan-water filling had been unsuccessful, it was not possible to convert the observed count rates directly into pressures of water vapour. The results could, however, be standardized by comparison with the vapour pressure measurements of Vierk, who reported values for dioxan-water solutions at 25°C in a composition range which just overlaps with the stronger of the two solutions studied here.

Alternatively the vapour pressure could be calculated from the count rate on the assumption that the counting efficiency of the dioxan-water filling is the same as that of the alcohol filling. Calculations based on this assumption gave partial vapour pressure values which agree fairly well with those of Vierk Fig. (37).

This rather unexpected agreement, and the apparently reasonable values of all the results, justify the initial assumption and suggest that the counting efficiency will not vary with the relative proportions of dioxan and water in the vapour phase.

The inconsistent results formerly obtained with this filling cannot be due to a variable efficiency, as was originally supposed. It is possible that the method of making up the fillings was at fault, large errors resulting from the adsorption of water on glass surfaces during the measurement of its pressure.

(iii) RESULTS

The partial vapour pressures measured in this way agree within 5% with known values and with other results obtained in this work by a more conventional method, Fig. (37), Table VIII.

The characteristics observed were in general worse for vapour containing smaller proportions of water Fig. (26). It seems possible that for dioxan solutions this method would cease to be useful for solutions of very low water content. This is probably because quenching by light adsorption cannot occur in dioxan, so there is no reason to suppose that this restriction is general.

Amore suitable apparatus for this work could be made from a maze counting tube, in which the cathode cylinder is outside the glass envelope. A flask could be joined directly to the bottom of the tube so that a larger volume of solution could be accommodated Fig. (38).

The vapour pressures measured by this method have not been used in the thermodynamic calculations in the next section.

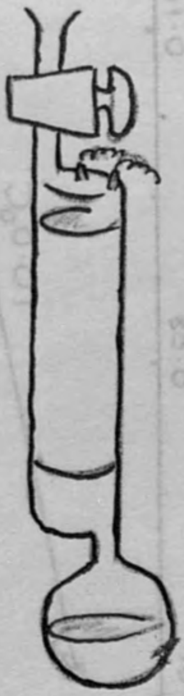


Fig. (38)

Correlation of Partial Pressure Measurements.

Figure (37)

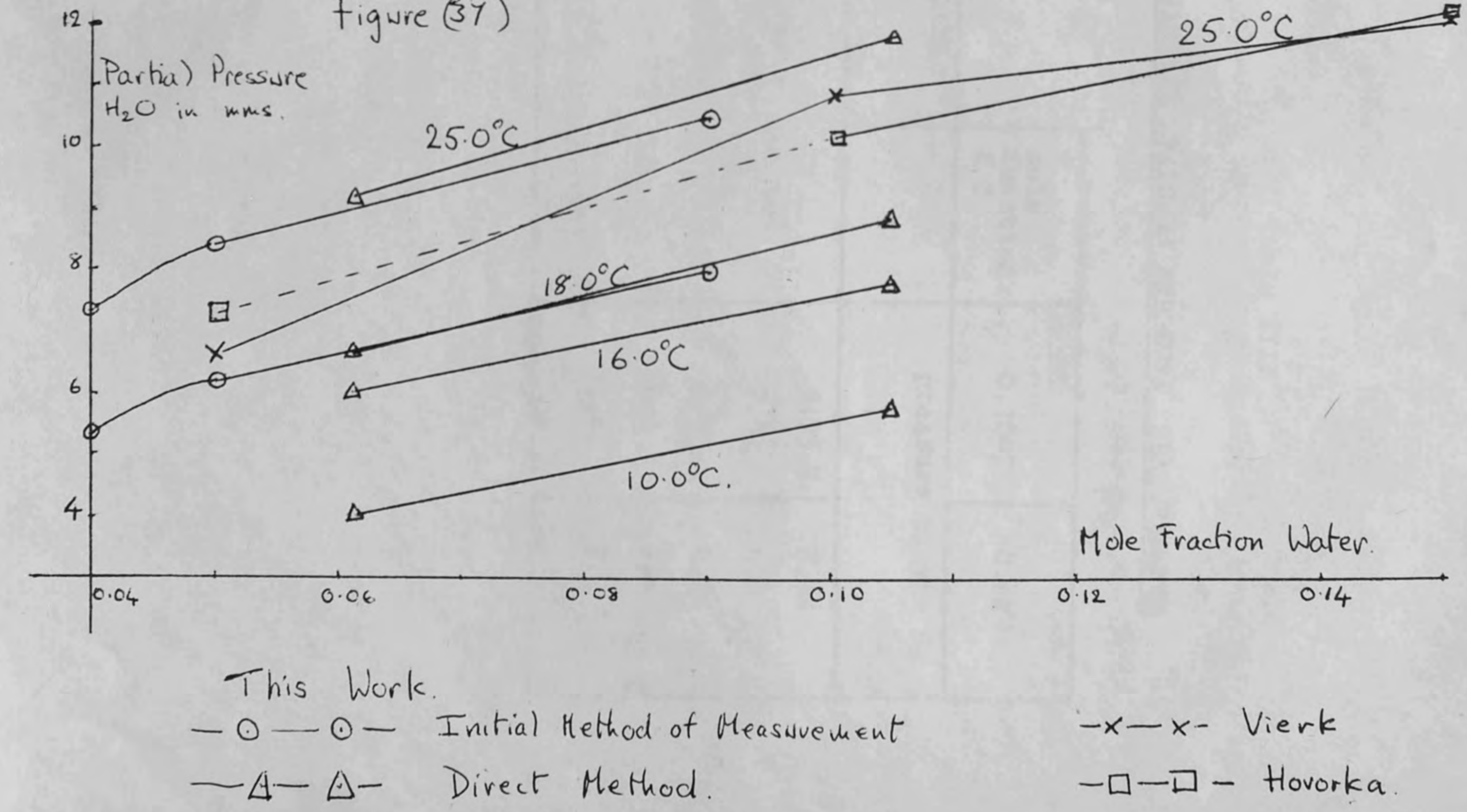


Table VIII

PARTIAL VAPOUR PRESSURE MEASUREMENTS

	mole fraction H_2O	0.1045	0.61
Temp. °C		pressure in mms Hg	
10		5.75	3.98
16		7.82	6.0
18·0		8.9	6.7
22		10.1	8.4
25.0		11.85	9.1

C. Thermodynamic Properties of Water in Dioxan-Water Solutions

I. The following properties of the system were calculated:

(1) Latent Heat of Evaporation

calculated from the Clausius-Clapeyron equation

$$H_a^V = \frac{RT_1T_2}{T_2-T_1} \log_e \frac{p_2}{p_1}$$

Table (X)
Fig. (39)

(2) Activity Coefficient

$$\gamma_a = \frac{p}{p^i}$$

Fig. (36)

where p^i is the ideal (Roault's Law) partial pressure.

(3) Excess Molar Free Energy of Mixing

$$G_a^E = RT \log_e \gamma_a$$

Table (IX) Fig. (40)

(4) Excess Molar Entropy of Mixing

$$S_a^E = -\frac{d\,(G_a^E)}{dt}$$

Table (IX) Fig. (40)

(5) Heat of Mixing

$$H_a^E = G_a^E + TS_a^\varepsilon$$

Table (IX) Fig. (40)

Calculation of the excess entropy and heat functions from the temperature coefficient of the free energy has the disadvantage that a small error in the measurement of the latter property yields a very large error in the entropy

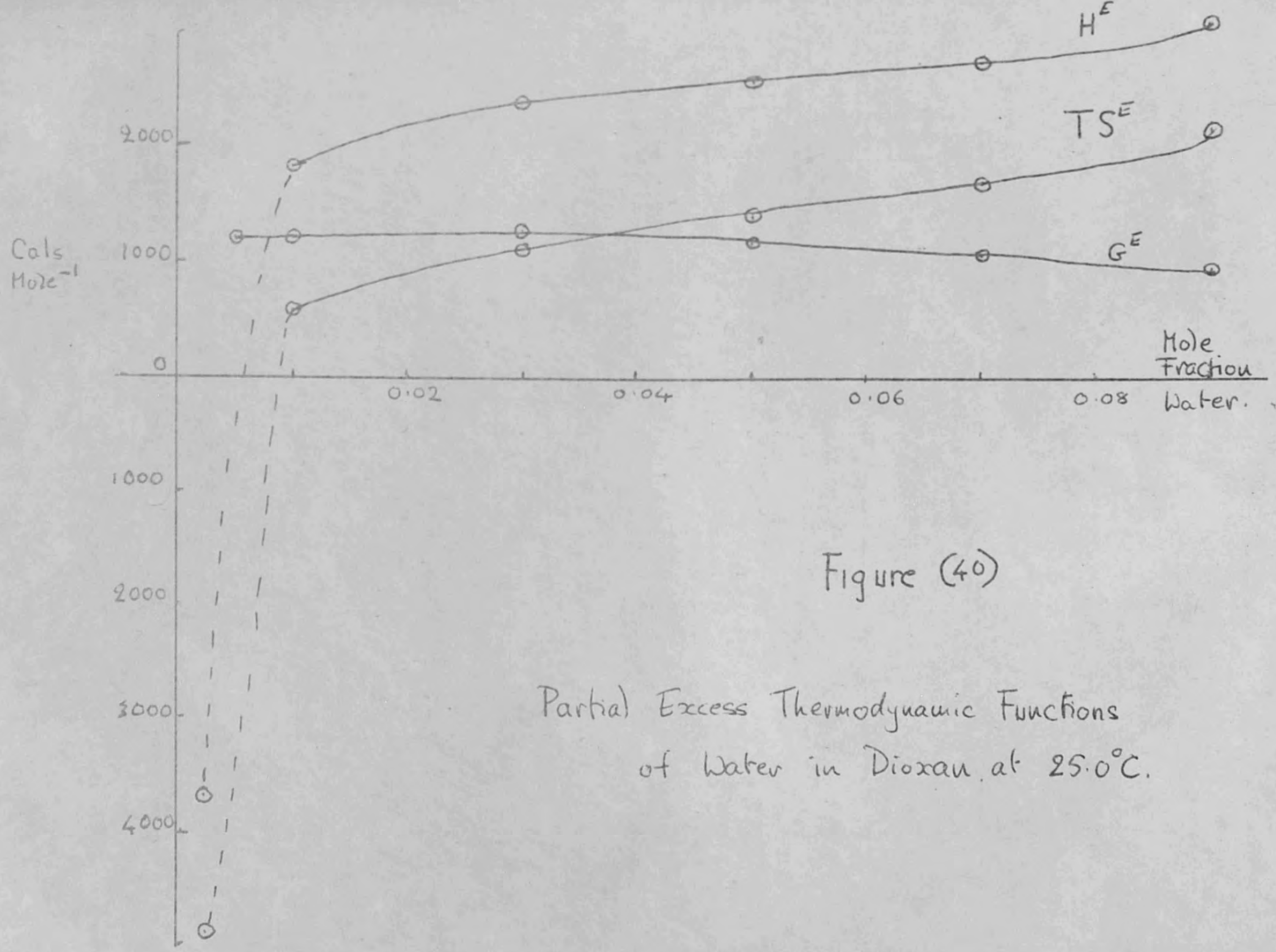


Figure (40)

Partial Excess Thermodynamic Functions of Water in Dioxan at 25·0°C.

Table (IX)

EXCESS THERMODYNAMIC FUNCTIONS OF WATER DIOXAN SOLUTIONS

mole fraction water	18°C calories per mole G^E	TS^E	H^E	25°C calories per mole G^E	TS^E	H^E
0.09	1003	2115	3118	952	2160	3113
0.07	1090	1660	2750	1050	1700	2750
0.05	1201	1365	2566	1168	1405	2568
0.03	1292	1076	2366	1266	1104	2370
0.01	1234	582	1816	1220	596	1816
0.005	1099	-4780	-3681	1215	-4890	-3675

and heat functions. Under the conditions of the present work, a 2% error in G_a^E results in a 30% error in S_a^E and a 15% error in H_a^E.

For this reason it is more usual to measure the heat of mixing independently by a calorimetric method and to derive the excess entropy from G^E and H^E.

This method has however the disadvantage that the excess heat and entropy functions thus obtained are total functions and the partial quantities which may be of greater interest cannot be obtained from them.

NOMENCLATURE USED IN FOLLOWING SECTIONS

Subscripts a and b refer to water and dioxan respectively. Thus H_a^E is the excess heat of mixing of water, while H^E without a subscript is the total heat of mixing of the solution.

The symbol x is used to represent mole fractions.

CALCULATION OF TOTAL EXCESS THERMODYNAMIC FUNCTIONS

The excess functions calculated from the partial pressures measured in this work refer to water only.

As it is usual to express the thermodynamic characteristics of non-ideal solutions as total excess functions direct comparison with published work on this system is impossible.

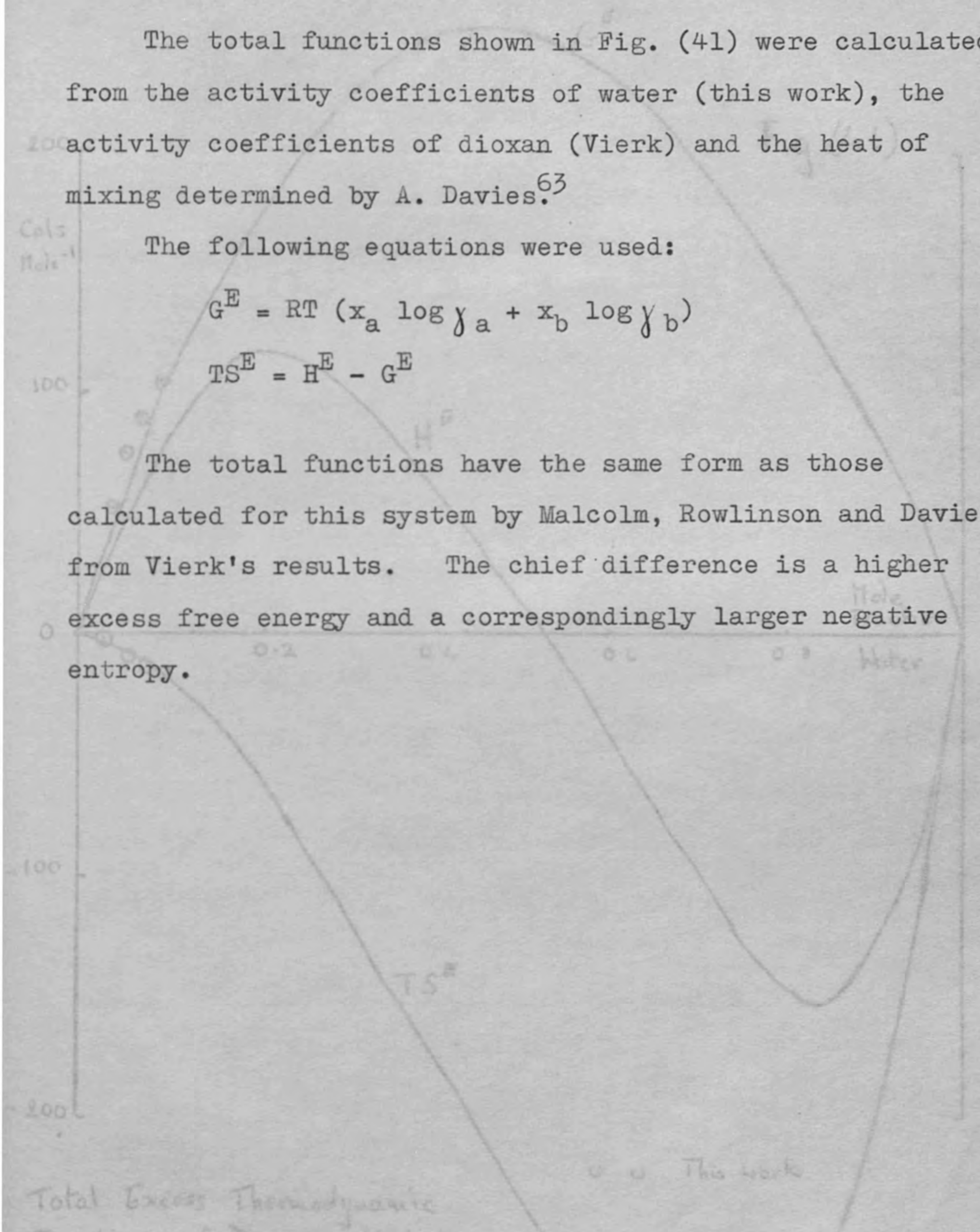
The total functions shown in Fig. (41) were calculated from the activity coefficients of water (this work), the activity coefficients of dioxan (Vierk) and the heat of mixing determined by A. Davies.[63]

The following equations were used:

$$G^E = RT\,(x_a \log\gamma_a + x_b \log\gamma_b)$$

$$TS^E = H^E - G^E$$

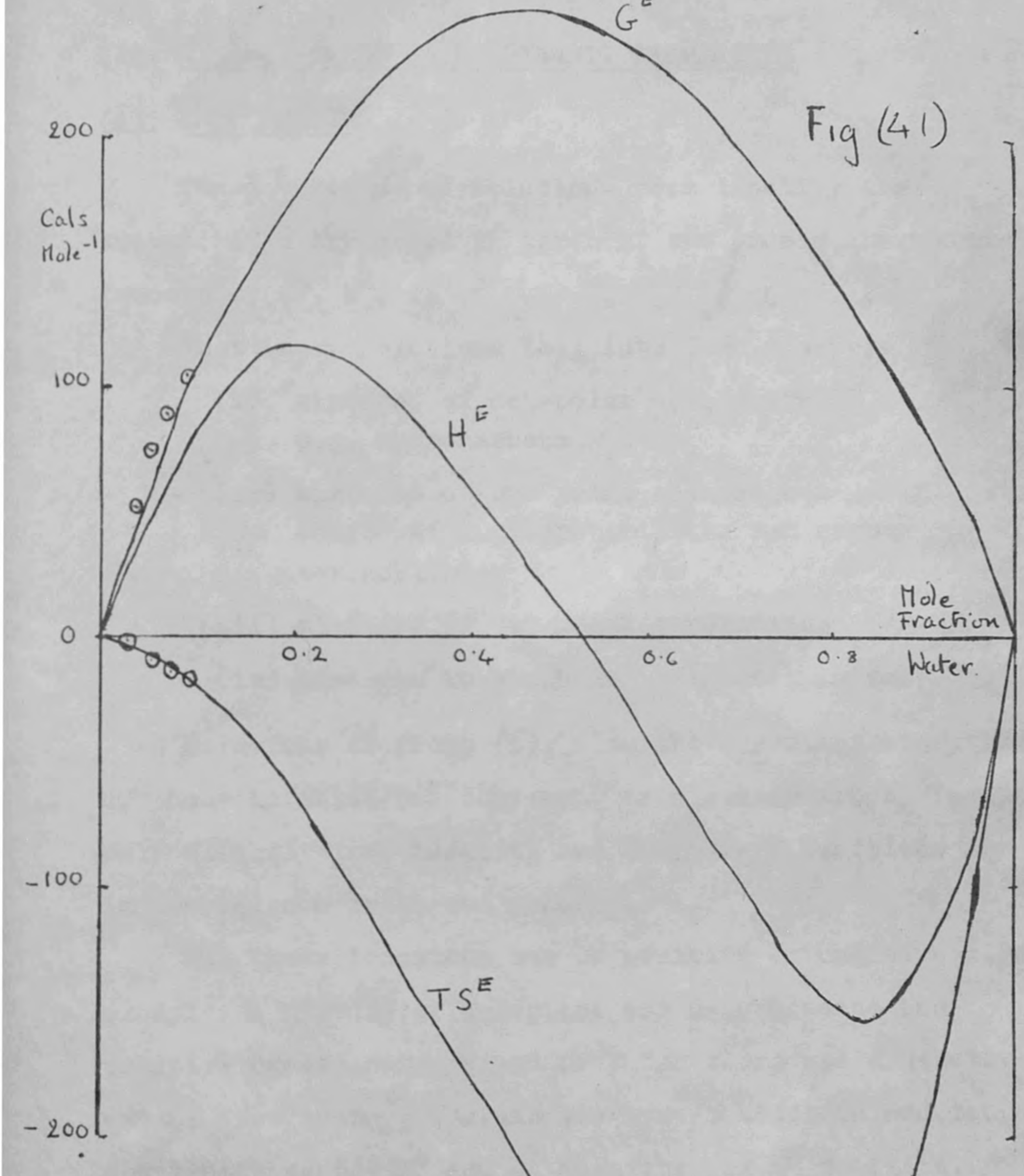
The total functions have the same form as those calculated for this system by Malcolm, Rowlinson and Davies[62] from Vierk's results. The chief difference is a higher excess free energy and a correspondingly larger negative entropy.



Total Excess Thermodynamic Functions of Dioxan-Water Solutions.

From the results of Vierk

Fig (41)



Total Excess Thermodynamic Functions of Dioxan-Water solutions.

From the results of Vierk.

C.

II. DISCUSSION OF THERMODYNAMIC PROPERTIES

(i) INTRODUCTION

The deviations of solutions from ideality are conveniently expressed in terms of the excess thermodynamic functions, G^E, H^E, TS^E.[56]

Most binary solutions fall into four groups:-

(i) mixtures of non-polar components e.g. hydrocarbons

(ii) mixtures of one polar and one non-polar component e.g. acetonitrile and carbon tetrachloride

(iii) mixtures of two polar components

(iv) mixtures in which one component is water

Solutions of group (i), with the important exception of those in which one component is a fluorocarbon, deviate only slightly from ideality and the excess functions are in consequence small and symmetrical.

All these functions can be positive or negative. For example, a mixture of n-heptane and n-hexadecane has positive excess entropy and heat functions and a negative excess free energy, whereas the system n-octane and tetra ethyl methane has H^E and S^E negative and G^E positive.

In neither system does the magnitude of any excess function exceed 40 calories per mole.

Solutions of group (ii) are less ideal and have therefore larger excess functions. The excess free energy, for example, in mixtures of carbon tetrachloride with acetonitrile or with methanol or ethanol is about 200 calories per mole.

The excess free energy and heat are usually positive and the excess entropy almost always negative. The positive excess heat is attributed to the separation of dipoles and in some cases to the disruption of hydrogen bonds. The negative entropy is probably due to a loose local structure imposed on the inert molecules in the solution by the dipole groups. This restricts the orientations of molecules so that mixing is not quite random.

The excess entropy sometimes becomes positive as the concentration of the polar component is reduced. This behaviour is exhibited by the solutions, ethanol-benzene,[60] methanol-benzene[59] and carbon monoxide-methane.[61]

Comparatively few solutions of group (iii) have been investigated so it is not possible to generalise concerning their excess functions.

Group (iv) solutions deviate widely from ideality because of the unique properties of water. The positive excess free energy is sometimes so high in aqueous solutions that phase separation readily occurs. A few aqueous solutions, notably those containing polyalcohols, have negative excess free energies. Aqueous hydrogen peroxide also has a negative excess free energy. The excess heat function may be positive or negative or it may be positive in one concentration range and negative in another. This characteristic is observed in dioxan-water solutions Fig. (41) and it can be explained in terms of the rupture of hydrogen bonds between water molecules at low concentrations of water and the formation of hydrogen bonds between water and dioxan at higher concentrations.[55]

The excess entropy of aqueous solutions is usually negative. This implies that hydrogen bonding persists in the solution and prevents random mixing. A further restriction of random mixing arises from the interaction between the permanent dipoles of water and dipoles induced in neighbouring molecules.

Spectroscopic Study of Solutions

The degree of hydrogen bonding in a solution can be directly ascertained by infra-red absorption spectrometry. Errara[65,66] and coworkers measured the infra red spectrum of solutions of ethanol and carbon tetrachloride and distinguished two hydroxylic absorbtion bands. One band corresponded to normal hydroxyl, i.e. to monomeric alcohol, and the other to hydrogen bonded hydroxyl, i.e. to dimers, trimers, etc., of alcohol. From the extinction coefficients of the two bands the degree of association of the alcohol can be calculated.

They found that a considerable proportion of alcohol was associated even at alcohol concentrations as low as 2% by volume.

(ii) EXCESS FUNCTIONS OF MIXING

The partial excess functions of water in dioxan solutions at 25°C are shown in Fig. (40). For ease of comparison with published work, in which total excess properties are given, the partial functions have been multiplied by x_a, the mole fraction of water, and plotted in Fig. (42).

The quantities shown in Fig. (42) are therefore the first terms in expressions of the type

$$G^E = RT\,(x_a \log_e \gamma_a + x_b \log_e \gamma_b)$$

which correspond to the total excess functions.

The thermodynamic functions lie on a smooth curve in the concentration range $x_a = 0.01$ to 0.09 but change abruptly when the mole fraction of water falls below 0.01. Discussion of this abnormally abrupt change is deferred to a later section.

The Excess Heat of Mixing

This quantity is positive i.e. heat is absorbed during solution. Absorption of heat is due to the rupture of hydrogen bonds and the separation of dipoles as water

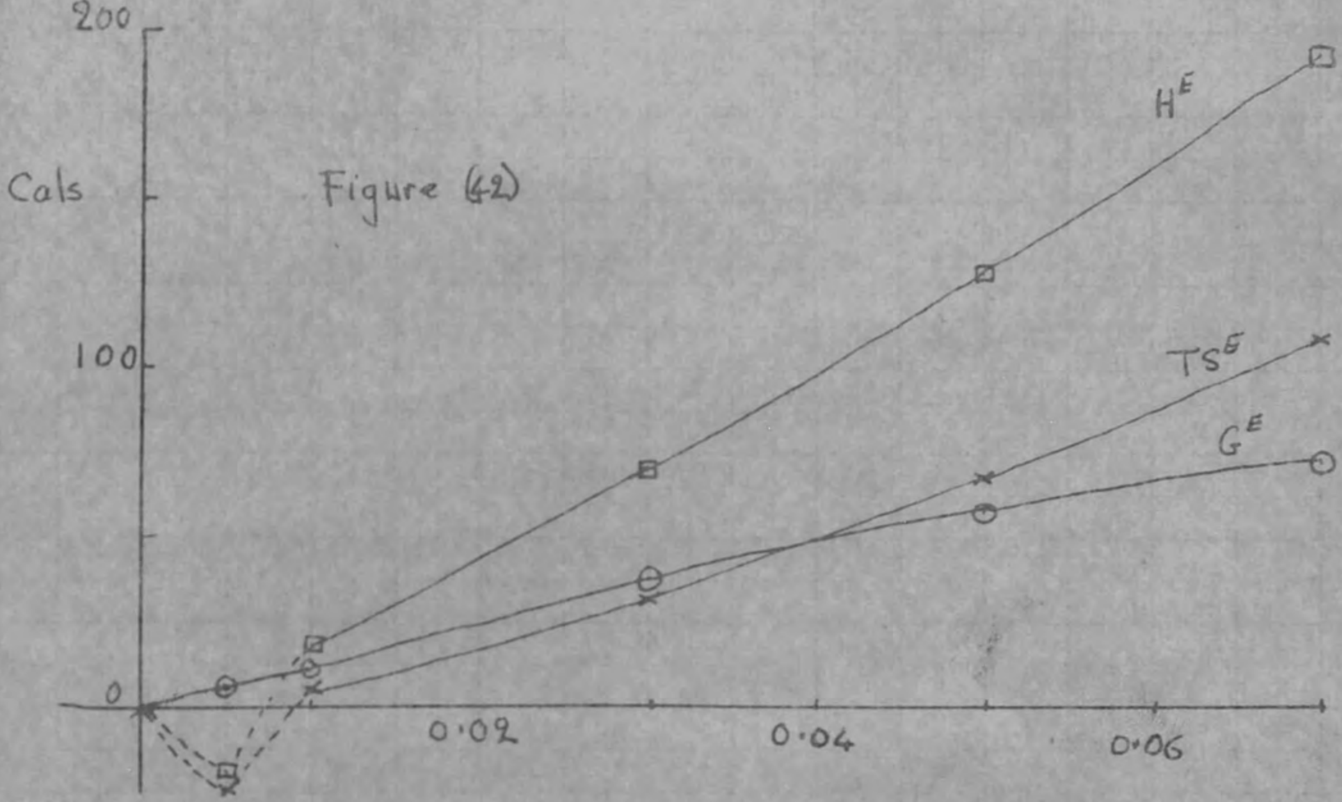


Figure (42)

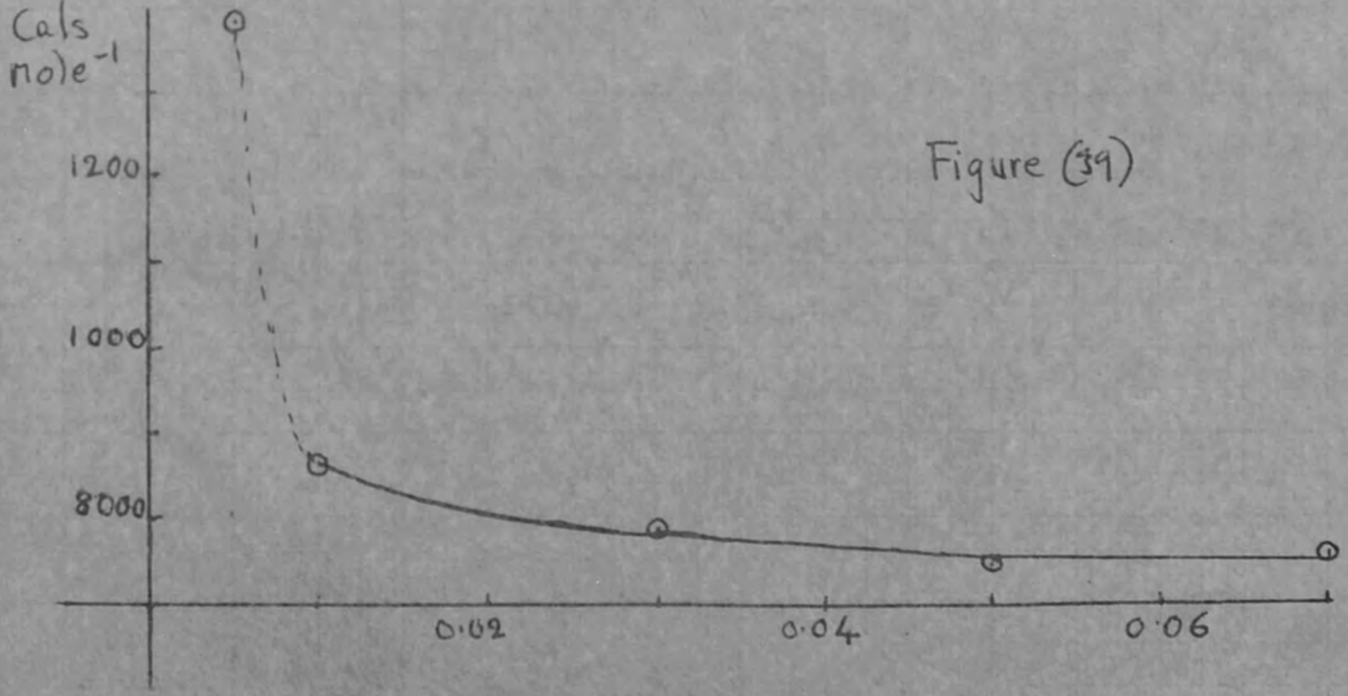


Figure (39)

Latent Heat of Vaporization of Water in Dioxan Solutions at 25.0°C molecules are dispersed in a large excess of dioxan. The magnitude of the heat term is only about a third of the heat of vaporization of water at 25°C which indicates either that multi molecular aggregates of water still exist in this solution or that rupture of hydrogen bonds between water molecules is partially compensated by the formation of hydrogen bonds between water and dioxan.

The slight increase of H^E with concentration of water is rather surprising as it would be expected that fewer hydrogen bonds between water molecules would be broken as the water content increases.

The total excess heat function also rises with concentration of water until $x_a = 0.2$. It then decreases and becomes negative when x_a exceeds 0.5. Fig. (41).

In order to account for this behaviour Rowlinson[55] postulated the formation of a hydrogen bond between dioxan and water. Thus, absorption of heat occurs in solutions weak in water because the predominating process is the separation of water molecules and the rupture of hydrogen bonds. In solutions of high water content bonds between water molecules are less frequently broken and the exothermic term due to the formation of dioxan-water hydrogen bonds predominates.

Association in ethanolic dioxan solutions has been studied spectroscopically by Huet, Philippe and Bono,[63] Their results, Fig. (43), show a surprisingly high degree

Association of Alcohol in Dioxan Solutions.

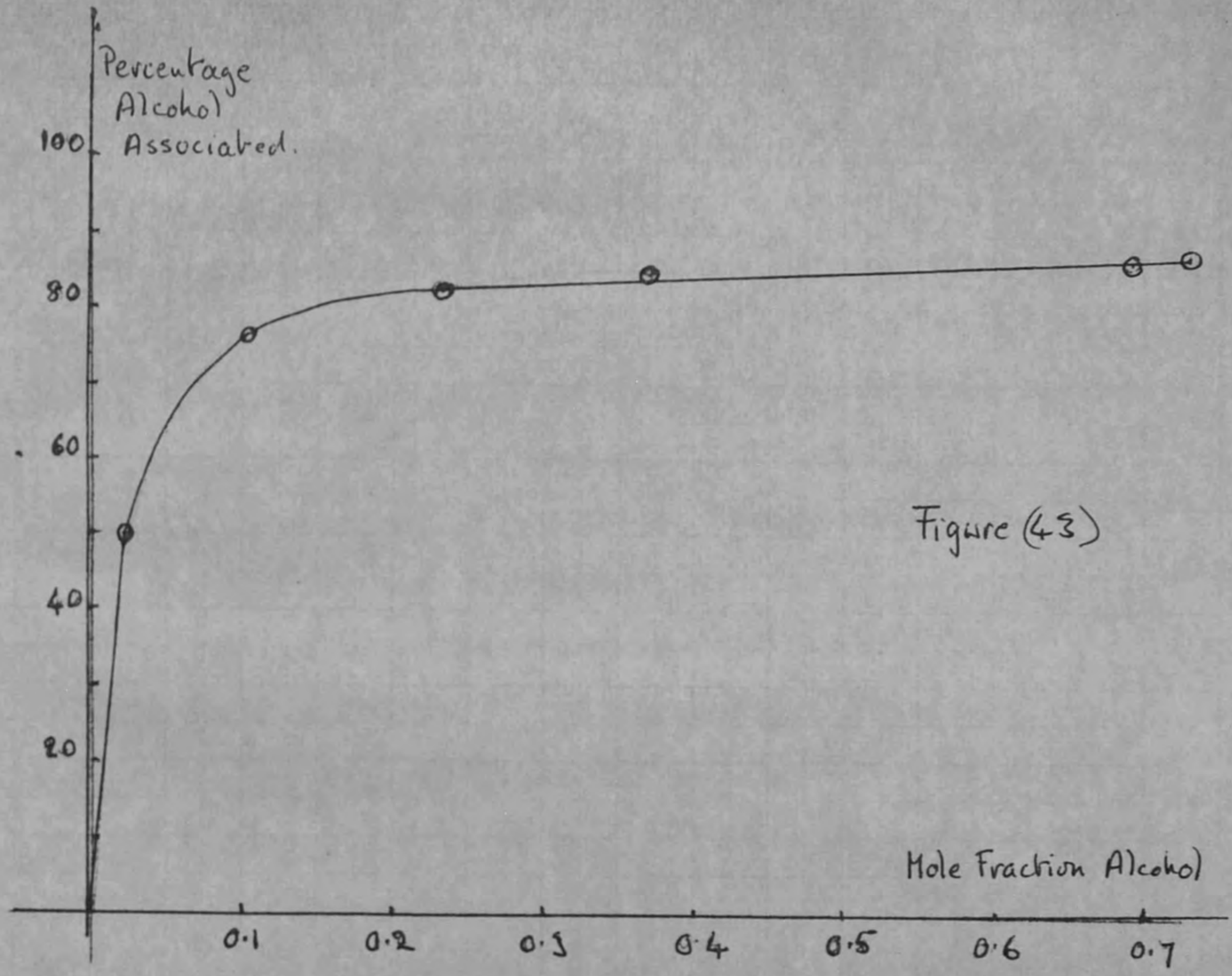


Figure (43)

From Bono, Philippe & Huet, Bull Soc. Chim Belg. 62. 442

of association in solutions containing as little as 0.022 mole fraction alcohol.

The behaviour of this system was quite different from that of methanol-carbon tetrachloride and ethanol-carbon tetrachloride which they also studied by the same method and is explicable if a strong interaction between dioxan and alcohol is assumed. As carbon tetrachloride cannot form hydrogen bonds it seems that the high degree of association observed in weakly alcoholic dioxan is due to hydrogen bonding between alcohol and dioxan.

It is probable that the same situation exists in weakly aqueous dioxan. The decrease in the activity coefficients, Fig. (36), as the mole fraction of water falls below 0.03 could be due to the disappearance of free water molecules, because mass action will favour the formation of water-dioxan complexes rather than water-water complexes as the mole fraction of dioxan approaches unity.

The Excess Entropy of Mixing

This quantity is positive, i.e. the entropy change is greater than that corresponding to random mixing. This is to be expected as the ideal entropy change, corresponding to random mixing

$$-\Delta S^I = R\,(x_a \log_e x_a + x_b \log_e x_b)$$

is calculated on the assumption that the pure liquids have no structure. As water has a definite structure its solution in another liquid will disrupt this and introduce an extra positive term into the entropy of mixing. The excess entropy term can therefore be positive even if random mixing is not attained due to continued association between some of the water molecules in the solution.

Conversely, it cannot be argued that the positive excess entropy indicates the complete dissociation of water into monomers.

A positive contribution to the entropy of mixing can also arise as a direct result of association. A statistical treatment of associated solutions has been proposed by Sarolea[64] and discussed by Prigogine and Defay.[57] His expression for the entropy of mixing in such solutions contains three terms, one expressing the orientational change and two, the configurational changes.

The orientational term is always negative because hydrogen bonding restricts the number of positions which a molecule can adopt relative to its neighbours.

The configurational changes which occur in associated solutions are

(i) a decrease in the total number of independent entities

and (ii) an increase in the number of different kinds of entities.

The first configurational term is always negative and usually predominates over the second, which is positive.

In some circumstances the second term may exceed the first.[57]

The total excess entropy is negative which is normal for aqueous solutions Fig. (41).

(iii) THE EXCESS THERMODYNAMIC FUNCTIONS BELOW $x_a = 0.01$

The excess free energy of mixing is an almost linear function of the concentration of water. At 18°C and at concentrations larger than $x_a = 0.01$, this quantity is greater than at 25°C. This is a consequence of the positive excess entropy discussed above.

Below $x_a = 0.01$ the two functions intersect and their relative magnitudes are reversed. The entropy and heat terms therefore become negative.

This seems a most improbable result as it means that water is more firmly associated with dioxan than it is with itself. The same conclusion has however been reached by Barcarella[45] from a study of the virial coefficients of the vapour of dioxan-water mixtures (p.47).

On the other hand there seems no reason why this phenomenon should reveal itself when the mole ratio of dioxan to water is 200:1.

(iv) EXPERIMENTAL ERRORS

An error of 20% in the pressure measurements is necessary to account for this anomaly. The standard deviation of all the pressure measurements is 4.84% and that of the measurements corresponding to the anomalous point is only 1.38%, so it seems rather unlikely that the inversion of the free energy functions is due to an error in pressure measurements.

If the probable error of the pressure measurements is assessed at 5% and if the errors at 18°C and 25°C are complimentary the total error of 10% reduces the heat and entropy functions to approximately -1200 calories per mole and -2400 calories per mole respectively.

If the anomalous result is due to experimental error the most probable source of the error is tritium contamination at some stage in the equilibration and assay of the solution at 25°C. As the quantity of tritiated water being assayed is of the order of 10 micrograms, contamination with 1 microgramme of a tritiated solution having ten times the activity would introduce an error of 100% into the pressure measurements. The same considerations apply to the abnormally high heat of vaporization found at this low concentration, Fig. (39). The possibility that this anomaly is due to an impurity in the dioxan cannot be excluded.

(v) SUGGESTED EXPLANATION OF ABNORMAL FUNCTIONS

If it is assumed that the inversion of the heat and entropy functions is not due to experimental error, a very simple explanation of this behaviour can be advanced.

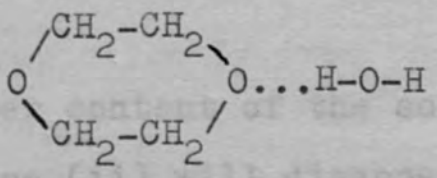
The Negative Excess Entropy

In solutions containing a sufficiently high proportion of water many different molecular species will be present.

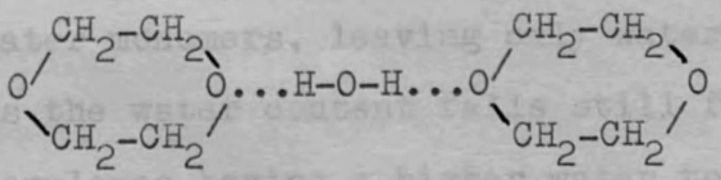
There will be:-

- (i) water monomers
- (ii) associated water, (dimers, trimers, tetramers, etc.)
- (iii) water associated with dioxan in various molecular proportions.

Innumerable complexes of type (iii) are possible because of the two oxygen atoms of the dioxan molecule. They include:-



(a)



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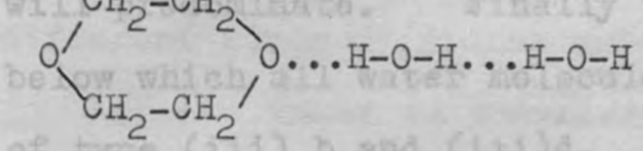
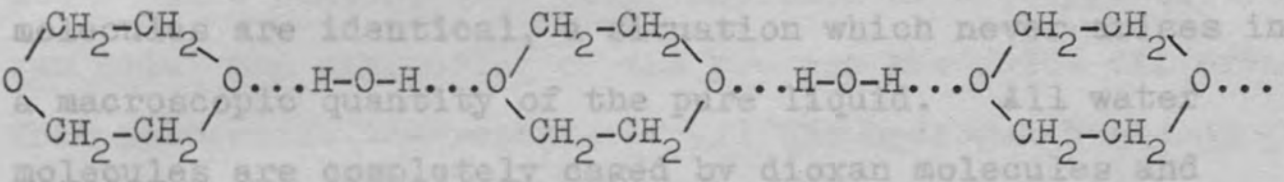
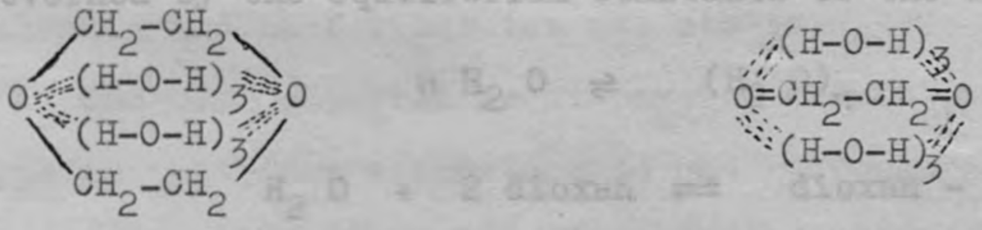


(c)



(d)

Many other types of dioxan water complex are obviously possible. A complex of six molecules of water and one of dioxan has been proposed by Coates and Sullivan.[58]



(e)

to account for the minimum of the total excess heat and entropy function in dioxan solutions having this concentration.

As the water content of the solution is reduced complexes of type (ii) will disappear first, followed by water monomers, leaving only water associated with dioxan. As the water content falls still further dioxan water complexes having a higher water to dioxan ratio will disappear and complexes of type (iii)a and (iii)b and (iii)d will predominate. Finally there must be a concentration below which all water molecules are present in complexes of type (iii) b and (iii)d. At this point all water molecules are identical, a situation which never arises in a macroscopic quantity of the pure liquid. All water molecules are completely caged by dioxan molecules and orientational, and configurational freedoms have been almost entirely lost.

A large loss of entropy therefore seems inevitable in the formation of very weak aqueous dioxan solutions. The concentration at which this change occurs must be governed by the equilibrium constants of the reactions:-

$$n\,H_2O \rightleftharpoons (H_2O)_n$$

$$H_2O + 2\text{ dioxan} \rightleftharpoons \text{dioxan} - H_2O - \text{dioxan}$$

The Negative Heat of Mixing

The explanation of the negative value of the heat of mixing follows directly from the nature of the complexes present.

If water is transferred from the pure liquid to a dioxan solution containing a sufficient proportion of water, some of the hydrogen bonds of water will be ruptured and heat will be absorbed. This is partly compensated by the formation of hydrogen bonds in many different kinds of dioxan water aggregates.

If now water is transferred into a solution of so low a water content that only complexes of the type (iii)b can exist the energetics of the process are quite different. This is because the rupture of all the hydrogen bonds of water always involves the breakage of less than two hydrogen bonds per molecule.

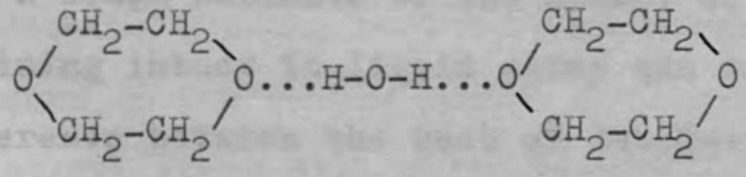
If, for the purpose of illustration, water is considered to be a linear aggregate of molecules -

...H-O-H...H-O-H...H-O-H...H-O-H...

rupture of any two hydrogen bonds completely liberates one molecule and half liberates two others.

The heat absorbed in dispersing a complex of this type is therefore equivalent to one hydrogen bond per mole.

If now the liberated molecules of water form complexes with dioxan of the type



two hydrogen bonds per mole are always formed. The net heat change during solution is therefore equivalent to the formation of one hydrogen bond per mole. If the contribution of Van der Waal's forces to the heat change are ignored, and if the hydrogen bonds are assumed to be equivalent and to have the value 5 Kcals per mole, the heat of mixing in very weakly aqueous dioxan solutions would be expected to have the value 5 Kcals per mole. Although the linear structure of water, which has been used here for the sake of clarity, is unreal the principle of the argument holds whatever the actual structure of water. The tetrahedral structure of liquid water proposed by Bernal and Fowler[67] is now generally accepted, but the number of hydrogen bonds linking each molecule to its neighbours is still not certainly known. In ice each water molecule is believed to form four bonds, two between its own hydrogen atoms and the oxygen of neighbouring water molecules, and two between the lone-pairs of electrons on its own oxygen atoms and the hydrogens of neighbouring water molecules. During fusion some of these bonds are broken, or distorted and weakened.[68]

A rough estimate of the number of hydrogen bonds remaining intact in liquid water can be made if the difference between the heat of sublimation of ice (12.2 Kcals at 0°C) and the heat of evaporation of water (10.3 Kcals at 25°C) is considered to be due primarily to the rupture of hydrogen bonds during the transition from solid to liquid.

Assuming the energy of the hydrogen bond to be 5 Kcals, the number of hydrogen bonds linking each molecule in liquid water at 25°C is 3.24.

The heat evolved if water forms complexes of type (iii)b should therefore correspond to the formation of 0.38 hydrogen bonds, i.e. the excess heat of mixing should be - 1.9 Kcals per mole.

In estimating the energy involved in the formation of the dioxan water complex, the possibility of hydrogen bonding between the lone-pair electrons of oxygen in the water molecule and the carbon bonded hydrogens of additional dioxan molecules has been neglected. Although hydrogen bonds of this type are weak there is considerable evidence that they exist. The heat of mixing chloroform and diethyl ether,[69] and chloroform and the dimethyl ether of ethylene glycol[70] are abnormally high, and hydrogen bond formation between the ethereal oxygen and the hydrogen atom in chloroform has been postulated to account for this. This kind of bond is believed to be favoured by electron withdrawing groups, in the above instances, halogen atoms, adjacent to the carbon bonded hydrogen. In dioxan the two oxygen atoms will withdraw electrons from the methylene group and enhance the electrostatic interaction between the hydrogen atoms and the lone-pair electrons on the oxygen atom of the water molecule. If this type of interaction does occur and complexes containing four molecules of dioxan and one of water are formed, the negative heat of mixing will be greater than the 1.9 Kcals calculated above.

Estimates of the strength of -C-H...O bonds range from 2.6 Kcals per mole for acetaldelyde[71] to 6 Kcals per mole for chloroform and diethyl ether.[69]

The explanation of the negative heat of mixing also explains the gradual increase in the positive heat of mixing as the water content is increased over the range $x_a = 0.01$ to 0.09. With increasing water content the proportion of the energetically stable 2.1 or 4.1 dioxan: water complexes decreases and many different types of dioxan water aggregate can form. This explains also the increasing entropy.

The abruptness of the change in the thermodynamic functions as the mole fraction of water falls below 0.01 remains very difficult to account for.

(vi) THE LATENT HEAT OF EVAPORATION

Fig. (39) shows the heat of evaporation of water in dioxan solutions as a function of the concentration of water. As would be expected from the positive heat of mixing this quantity is smaller than that for pure water.

The consistency of these results is indicated by Table (X) which shows that the sum of the heat of evaporation H_v and the heat of mixing, H^E, is at all concentrations fairly close to the accepted value (10.3 Kcals mole^{-1}) for the heat of evaporation of pure water at 25°C.

Mole Fraction Water	H_v	H^E	H_v+H^E
0.07	7.563	2.750	10.313
0.05	7.454	2.568	9.95
0.03	7.84	2.37	10.21
0.01	8.64	1.80	10.44
0.005	13.86	-3.68	10.18

Table X.

The heat of evaporation at $x_a = 0.005$ is well above that for pure water. The possibility that this anomaly is due to experimental error is governed by the same factors which have been discussed on p.88

The probable experimental error of these results is about 20%, which is insufficient to account for the latent heat exceeding that of pure water.

The high value is readily accounted for if all the water is present in the form of a complex with two molecules of dioxan. Two hydrogen bonds have then to be broken in order to liberate one molecule of water.

The situation is in this respect analogous to that of ice were each water molecule is linked by four hydrogen bonds to its neighbours. The heat of sublimation of ice is 12.2 K cals.

CONCLUSION

This research has resulted in the development of two methods for the measurement of low partial pressures of water in dioxan.

In the first method, the water content of the vapour phase is determined after equilibration using a new and simple technique of tritium assay.

In the second method, the partial pressure of water is determined by direct measurement of the radioactivity above a solution.

Further work remains to be done in improving these methods and in applying them to partial pressure measurements in other systems.

POSSIBLE IMPROVEMENT OF ASSAY METHOD

This technique is subject to the following errors:-

(i) Statistical

(ii) Manometric

(iii) Variability of Dead-Time with water content, pressure of filling and temperature of counting.

The statistical error is common to all radioactive methods and can be reduced at will by increasing the time of counting. The error in measuring the pressure of alcohol introduced into a Geiger tube can be reduced by substituting an oil manometer for the conventional mercury filled type, or by working with higher pressure fillings. The latter alternative would be advantageous because the Geiger characteristic improves with increasing pressure. It could be achieved by enclosing a small part of the vacuum line in a heated compartment and raising the temperature at the lead castle so that condensation would not occur during counting.

A more comprehensive investigation of the effect of water, pressure and temperature on the dead-time of the discharge would be desirable. Alternatively a probe unit with a dead-time longer than that of the discharge could be incorporated in the counting circuit.

Additional errors may result from the fast exchange of tritium between hydroxyl groups. Loss of activity can occur by exchange with atmospheric water vapour, adsorbed water on glass, and hydroxylic groups in the glass. Abnormally high results will be obtained if glass apparatus has been contaminated with high activity tritiated water.

Exchange with atmospheric water vapour can be prevented by vacuum manipulation throughout, exchange with hydroxylic groups in the glass can be reduced by coating the glass with silicone polymer; but the removal of all adsorbed water from all glass apparatus is a formidable problem. A thorough investigation of the errors arising from exchange with adsorbed water is necessary if the full sensitivity of tritium tracer work is to be exploited.

POSSIBLE IMPROVEMENT OF DIRECT METHOD OF MEASURING VAPOUR PRESSURE

The method described in Section B. IV gave unexpectedly good results. It would be of interest to establish the accuracy of this technique using a specially modified Geiger tube, and to apply it to other systems. One important point which requires investigation is the variation of the dead-time of the Geiger discharge with the composition of the vapour.

POSSIBLE EXTENSION OF PRESENT WORK

Further work is necessary to extend the thermodynamic data for the dioxan-water system into a concentration range still weaker in water. In particular it would be desirable to confirm or reject the abnormal heat and entropy terms found in this work.

Infra red spectroscopy might be of great value in interpreting the thermodynamic data derived from the pressure measurements. It should for example be possible to show whether or not free water monomers exist and, if they do exist, to relate their concentration to the total water content of the solution. If there is a detectable difference between the frequencies of the absorption bands of hydrogen bonds between two water molecules and a water molecule and a dioxan molecule it might also be possible to estimate the relative proportions of water-water complexes and water-dioxan complexes.

The assay method described in this work could also be used, without any modification, for the measurement of low partial pressures of alcohols. The alcohol could be labelled either with tritium or with carbon -14, but the use of the latter would be advantageous because the difficulties associated with tritium assay, notably exchange and contamination, would not arise.

Thermodynamic data for weakly alcoholic solutions in dioxan and other solvents should therefore be readily accessible by the methods described.

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