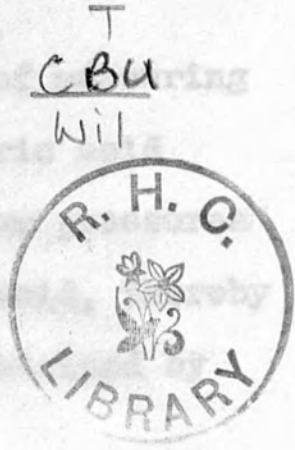


VAPOUR PRESSURES OF
AQUEOUS SOLUTIONS



A thesis submitted by Randall Gordon
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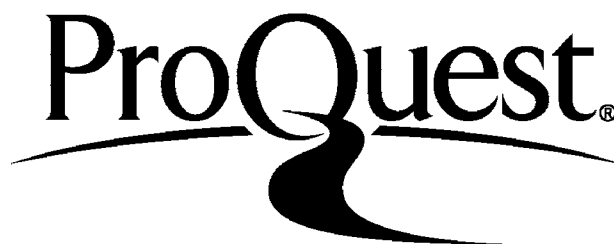
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Abstract

The dynamic air saturation method of measuring vapour pressures has been applied to sulphuric acid solutions at 25°C. The partial water vapour pressures have been determined in the range 45 - 95% acid, thereby confirming and extending previous results obtained by direct static measurements.

The application of a radioactive tracer technique to the air saturation method of determining vapour pressures has been successfully accomplished. The calculated activities obtained in the more concentrated acid region were found to be in moderate agreement with previous values obtained from indirect measurements.

A new method of tritium assay involving β -phase gas counting of tritiated alcohol has been developed and substantiated.

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INTRODUCTION

The water vapour pressure over the system sulphuric acid - water has been determined by relatively few workers in the past. The reason for the lack of work in this direction probably lies in the practical obstacles encountered in this field, and also the difficulty in interpreting the results obtained.

Vapour pressure measurements are of importance in that the data obtained can be used in the calculation of activity values. If a liquid and vapour are in equilibrium, the chemical potential of any given component will be the same in both phases. It can be shown that the chemical potential of any component in a liquid solution may be represented by

$$\mu = \mu^0 + RT \ln p \dots\dots\dots(1)$$

where p is the partial pressure or, more correctly, the fugacity of the component in the vapour in equilibrium with the solution. If the solution is

ideal, then the partial pressure, or fugacity, is proportional to the mole fraction (x) of that constituent of the solution; hence equation(1) becomes

$$\mu = \mu^{\circ}x + RT \ln x \dots\dots\dots(2)$$

in then p_1° it follows that

For a non ideal solution, it is necessary to modify equation (2) by introducing an activity coefficient (G. N. Lewis 1901), thus

$$\mu = \mu^{\circ}x + RT \ln xf \dots\dots\dots(3)$$

where f approaches unity as the system tends towards ideal behaviour. The product xf is called the activity of the particular component and is represented by the symbol a ,

$$\text{thus } a = xf \dots\dots\dots(4)$$

$$\text{and } \mu = \mu^{\circ}x + RT \ln a \dots\dots\dots(5)$$

Now if the vapour is assumed to behave as an ideal gas, then it follows that both equations (1) and (5) represent the chemical potential. Hence it may be said that the activity of the solvent (a_1) in a solution is proportional to its partial

conditions it is certain that the total pressure
vapour pressure (p_1)

i.e. $a_1 = k p_1$ sulphuric acid being considered as a
non-volatile component. If the temperature is

Now in a pure liquid the activity of
the solvent is unity and since the vapour pressure
is then p_1^0 it follows that

$k = 1/p_1^0$ will also increase. It still

and hence $a_1 = p_1/p_1^0$ the system is complicated by

the dissociation of the sulphuric acid into sulphur
trioxide and water.

If the partial vapour pressure of water
over the system $H_2O - H_2SO_4$ is measured at $25^\circ C$ then

$$a_w = p_w/p_w^0$$

where a_w = activity of the water molecule

p_w = partial vapour pressure of water

p_w^0 = vapour pressure of water at $25^\circ C$.

One of the earlier reports in the literature
is given by Regnault (2) who measured the total
vapour pressure over sulphuric acid solutions for
temperatures from $5^\circ C$ to $35^\circ C$, and for concentrations
ranging from 24.26 to 84.48% H_2SO_4 . Under these

conditions it is certain that the total pressure over the system is that exerted by the water vapour, the sulphuric acid being considered as a non-volatile component. If the temperature is increased it follows that the sulphuric acid should itself exert an appreciable vapour pressure. If the concentration of the acid is increased its partial pressure will also increase. At still higher temperatures, the system is complicated by the dissociation of the sulphuric acid into sulphur trioxide and water.

Sorel (3) determined the total vapour pressure over sulphuric acid solutions up to 95°C and for concentrations up to 83% H_2SO_4 : his method consisted of passing an accurately measured volume of air through the sulphuric acid solution. Also, it maintained at a constant temperature, and collecting the water vapour carried over in absorption tubes. The vapour pressure was calculated from the formula

$$p = 6229 \frac{gT}{m (v + 6229T/mb)}$$

method as Sorel (3) and extended the latter's

where

p = Vapour pressure in mm.Hg.

g = Weight of water vapour absorbed.

v = Volume of air passed through saturator.

T = Absolute temperature in $^{\circ}\text{K}$.

M = Molecular weight of vapour.

b = Barometric pressure.

The term $6229 \frac{gT}{mb}$ is a correction for the volume of vapour carried over, and is the volume of vapour reduced to the same pressure as that under which the air was measured.

The limitations of this method are fairly obvious because should the acid exert an appreciable vapour pressure, then the pressure recorded would not represent that of the aqueous vapour. Also, it would not represent the total vapour pressure over the system because the vapour would be of an unknown composition and hence the value of the molecular weight used in the formula would be in error.

Briggs (4) employed the same "air saturation" method as Sorel (3) and extended the latter's

observations up to 200°C and for concentrations ranging up to 91% H_2SO_4 . The difficulties experienced by Sorel (3) in his work were here increased and the accuracy rendered still more uncertain because of difficulties in maintaining constant temperatures.

Burt (5) commented on these assumptions and measured the total vapour pressure over the system employing a dynamic method. A modification of an apparatus designed by Innes (6) was used, whereby the sulphuric acid solution was boiled under various pressures, temperature and pressure being accurately recorded. The work was carried out over a concentration range of 24.92-95.94 H_2SO_4 and a temperature range of 55°C - 235°C . He pointed out that at the higher temperatures, and especially in the more concentrated solutions, the acid might exert an appreciable vapour pressure; nevertheless, in his calculations, the vapour is considered to be that of water only.

Thomas and Ramsay (7) measured the partial pressure of sulphuric acid in solutions containing

from 86-99.6% H_2SO_4 and at temperatures from $160^{\circ}C$ to $260^{\circ}C$. They employed an air saturation method based on that of Foote and Scholes (8). They pointed out that this particular method had been severely criticised by Carveth and Fowler (9) but had also been adequately defended by Perman (10). They employed a new method of determining the quantity of acid vapour in the air stream by passing the latter through conductivity water. By using the figures on specific conductivities of sulphuric acid solutions obtained by Whethman (11), they were able to calculate the weight of the acid carried over in the air stream. The partial pressure exerted by the water vapour was not determined.

All of the work being carried out at this time was on more concentrated acid solutions.

Grollman and Frozer (12), using the isothermometric vapour pressure method as first described by Frazer and Lovelace (13), measured the water vapour pressure at $25^{\circ}C$ for dilute solutions, i.e. up to three molal. From the values so obtained they were able to calculate the activity coefficients for the sulphuric acid.

Previous workers had measured the partial pressure of the water vapour, the partial pressure of the sulphuric acid vapour, or the total pressure over the system. Thomas and Barker (14) obtained these individual values using fundamentally the same method as Thomas and Ramsay (7). The range completed was 89-99.3% H₂SO₄ and 180-300°C.

Thomas and Barker (14) were also able to show that the results obtained by Thomas and Ramsay (7) were uniformly low. Two sources of error were revealed on investigation: (a) the adsorption of the sulphuric acid on the glass wool, which had been introduced between the saturator and the absorption tube in order to remove spray, and (b) the possibility of the acid solutions not being in thermal equilibrium with the thermostat.

Earlier vapour pressure measurements, excepting those of Regnault (2), Sorel (3) and Brønsted (15), had been carried out at temperatures well above 25°C. This necessitated the use of partial thermo-

dynamic quantities if the pressure at 25°C was to be determined. Unfortunately, the measurements of the latter quantities were sparse and not very reliable.

After making a survey of the different methods of measuring vapour pressure, Wilson (15) decided McHaffie (16) attempted to measure the water vapour pressure over the system at 25°C and in the concentration range of 65.9-83.5% acid. He employed the dynamic air saturation method of measuring the vapour pressures and developed a technique (17) for determining the weight of the water carried over in the air stream. The results obtained were in good agreement with those calculated by Wilson (18) and measured by Bronsted (15), Sorel (3) and Briggs (4).

only moderate agreement.
McDougall and Blumer (19) in their studies of the system sulphuric acid-water-acetic acid were able to measure the lowering of the vapour pressure by a method based on the original apparatus of Washburn and Heuse (20). The determinations were carried out at 25°C but the sulphuric acid concentration was limited to 0.14-2.18 molar, no acetic acid being present in this range. Activity co-

efficients for the sulphuric acid were calculated from the data obtained.

After making a survey of the different methods of measuring vapour pressure, Wilson (18) decided that the static methods had provided the most self-consistent and reliable results. Selecting a modified form of the isoteniscope of Smith and Menzies (31), he measured the total vapour pressure over sulphuric acid solutions up to 70% acid and in the temperature range of 20-140°C.

This total vapour pressure data, which was assumed to be the water vapour pressure, when compared with Hepburn (32) and Greenewalt (33) was found to be of only moderate agreement.

Collins (23) determined the aqueous partial pressures over sulphuric acid solutions for concentrations up to 70% H_2SO_4 and from 20-140°C. An isoteniscope was devised so that the vapour pressures of solutions could be measured with no accompanying change in the concentration of the acid. For the concentrations from 30-65% acid at 25°C, the probable

error was assessed at not more than 0.3%. The pressures for 70% acid were obtained by extrapolation and were probably not better than 1%. Collins (23) compared his values at 25°C with those of Hepburn (32), Wilson (18) and Greenewalt (33). Up to 45% acid the agreement was good ($< \pm 1\%$) but beyond this it tended to deteriorate ($\pm 10\%$). The heats of vaporization of water from solutions of the above range of concentration (21) were found to be consistent with those of Brillouin and Franey (12) and Collins (23). They were

Shankman and Gordon (21) required a reliable standard for the isopiestic method of investigating the thermodynamic properties of aqueous solutions. Sodium chloride had been used in dilute solutions but could not be employed for solutions in which the activity of the water was less than 0.75. Sulphuric acid was selected as the most appropriate standard and the vapour pressures of the acid solutions at 25°C for concentrations from 2-23 molal were measured. The method adopted was similar to the static one of Gibson and Adams (22), whose claims to its convenience and accuracy were confirmed. They were able to

partial pressures over a wide range of concentrations

previous workers produced results in a limited measure the vapour pressure of the solutions, the vapour pressure of the solvent and the differential vapour pressure lowering. Accurate temperature control to within 0.01°C was maintained and the general care taken in the operation of the apparatus was emphasised.

The results obtained by Shankman and Gordon (21) were found to be consistent with those of Grollman and Frazer (12) and Collins (23). They were also in very good agreement for solutions of concentrations up to three molal with water activities calculated from e.m.f. measurements by Harned and Hamer (24), but beyond this the deviations lay well outside the experimental error and were as high as 4.5% at sixteen molal. When compared with data obtained by Scatchard, Hamer and Wood (25), agreement is excellent up to three molal and even beyond this the discrepancies are never greater than 0.3% in activity values. It is of importance to note that Shankman and Gordon (21) succeeded in producing a very accurate set of data on water activities and hence partial pressures over a wide range of concentration;

previous workers produced results in a limited range of concentration or at much higher temperatures.

Although the differential method of measuring the vapour pressures provided a consistent set of data on sulphuric acid, the calculated activities did not compare favourably with those obtained by the isopiestic methods (27). Robinson (30) attempted to clarify the position by further isopiestic studies on sulphuric acid and lithium chloride solutions, the latter already having been accepted as a reference solution following the work of Gibson and Adams (22). Measurements were made at 20.28°C and had to be corrected to 25°C . The corrected results were found to be unsatisfactory when compared with those of Shankman and Gordon (21) or Harned and Homer (24).

Stokes (28) attempted to clarify the position by using a completely different method of measuring vapour pressures. The method, originally used by Weir (29) consisted of establishing a steady state

by distillation between the solution at 25°C and pure water at a known lower temperature. When equilibrium is attained it follows that the pressures exerted by each system must be equal. The solution was rapidly removed from the evacuated apparatus and poured into a tared weighing bottle. The concentration of the equilibrium solution then determined by analysis of the weighed portion.

Stokes (28) compared his results with those of Shankman and Gordon (21) by computing two deviation functions x_1 and x_2 where

$$x_1 = a_w + 0.0754 m$$

between three and seven molal, and

$$x_2 = a_w + 0.05 m - 0.0035 (m - 10.5)^2$$

between six and twelve molal.

a_w = water activity.

A plot of molality (m) versus x_1 (range 3-7 molal) gave a smooth curve which compared favourably with similar plots of Shankman and Gordon (21) and Olynk and Gordon (26), the water activity

differing only in the fourth decimal place. At the higher concentrations (7-12 molal) the water activities appear to be consistently higher than those of Shankman and Gordon (21), the average difference being 0.0008 in the activity range of 0.5393-0.2935.

Stokes (28) pointed out this difference and suggested that his results were more acceptable on the grounds that the scattering of the points from the curve was less than those of Shankman and Gordon (21). It is also pointed out that the results of Shankman and Gordon (21) were obtained by direct measurements of vapour pressures while the data of Olynk and Gordon (26) and Stokes (28) were obtained indirectly, to the extent that they involved isopiestic comparisons between sulphuric acid and reference solutions whose vapour pressures had been independently determined. These isopiestic comparisons would not introduce errors of the magnitude that are found and hence one set of data is probably in error. The activities as calculated by

Harned and Hamer (24) in their e.m.f. measurements were found to differ by as much as 0.0060 in the activity range of 0.8700-0.8500 (6-13 molal). Stokes (28) had little doubt in concluding that these results were wrong, but was unable to account for errors of this magnitude.

An interesting feature of these results was the fact that even though there were discrepancies in the vapour pressure measurements, the results were generally in much better agreement than those obtained by electromotive force measurements, especially in the more concentrated acid region.

Abel (34) became interested in the problems related to aqueous sulphuric acid solutions and made a very complete survey of all previous work connected with this acid. From the mass of data published, and on the basis of thermodynamic relationships, he was able to derive an expression for the partial vapour pressure of H_2SO_4 (p_π) in the vapour phase above the liquid solution (πH_2SO_4). It was of

the form

$$\log p_{\pi} = A_{\pi} + \frac{B_{\pi}}{T} + D_{\pi} \log T + E_{\pi} T$$

The coefficients of this vapour pressure formula were calculated from the activity of the sulphuric acid component at a given temperature (298°K) in its dependence on concentration (π); from the dissociation constant of sulphuric acid vapour in its dependence on temperature, and from various thermal data which had been obtained from the literature. The constant A_{π} , which is a function of concentration, contains a term independent of the concentration; this latter term contains the entropy of formation of H_2SO_4 in its standard state from H_2O (g) and SO_3 (g) in their standard states. From the sparse observations given in the literature on the vapour pressure of sulphuric acid above the system $H_2SO_4-H_2O$, a constant was obtained, the value of which was in agreement with that of the entropy of formation. Because of the uncertainty in accuracy of the thermal data appearing in the literature, Abel (34) was forced to make approximations in his thermodynamic treatment,

but succeeded in producing valuable data over a wide range of concentration and temperature.

A section of Abel's (34) original calculations were based on the formation of sulphuric acid in its standard state $(\text{H}_2\text{SO}_4)^0$ from sulphur trioxide SO_3^0 (g) and water vapour H_2O^0 (g) in their standard states. Partial molal heat contents and capacities, previously calculated indirectly, were determined experimentally by Craig and Vinal (36). As a result of these new data, a more reliable relation was proposed for the sulphuric acid partial pressure over the system H_2SO_4 - H_2O in its dependence on concentration and temperature.

Another report (37) followed the appearance of fresh data on the free energy of sulphur trioxide. Sulphuric acid partial pressures at 25°C were tabulated over the concentration range 10-85% acid.

A new point on the concentration - vapour pressure scale was reached when Hornung and Giaque (38) made direct observations of the vapour pressure of water over $\text{H}_2\text{SO}_4 \cdot \text{A}\text{H}_2\text{O}$ where $\text{A} = 4, 3$ and 2 . The

observations were carried out at 25°C and above. This necessitated the use of partial molal heat content and capacity data in order to calculate the vapour pressure at 25°C. These data were available (39) and were stated to be of high accuracy. The results obtained agreed closely with those of Stokes (28) and even more so with those of Shankman and Gordon (21). They were found to be approximately 0.2%, below those of Shankman and Gordon (21), but this was accounted for by discrepancies in the methods used in standardizing the acid solutions. A very accurate method of standardizing sulphuric acid solutions (40) was referred to.

In 1951 Jones (41) described an apparatus by which the aqueous vapour pressure of a solution or substance could be determined to within 0.07 mm.Hg. The method consisted of measuring the change in volume, at constant temperature and pressure, of a sample of air in equilibrium with the solution after absorption of the water vapour in it by concentrated sulphuric acid. Results were recorded for the water vapour pressure in the temperature range 17.28-23.14°C.

Equilibrium humidities of solutions of H_2SO_4 at 25°C over a range of concentration 5-85% were also recorded and compared with published work. Jones (41) computed a series of "best values" from the work of Abel (34), Stokes (28), Shankman and Gordon (21), Harned and Hamer (24), Hepburn (32) and Wilson (18), and suggested that they were accurate to within $\pm 0.08\%$ relative humidity. The comparison of the experimental figures with the "best values" showed that, of the twelve results, nine had errors less than 0.25%, two were low by 0.3% and one by 0.4% relative humidity. No explanation was offered for these rather low results.

Deno and Taft (42) claimed that the H_0 function of Hammett (43) could be evaluated from 83-99.8% sulphuric acid and the activity of the water estimated to a reasonable agreement with experiment from 83 to at least 95% acid. The method assumed that the reaction



was of primary importance in determining the properties of these solutions, and a mole fraction

equilibrium constant of 50 was shown to be applicable for the entire range 83-99.8% sulphuric acid.

The logarithms of the activities calculated were compared with measured data of Shankman and Gordon (21), and with those of Thomas and Barker (14) and Burt (5); the vapour pressure data of the latter two were extrapolated to 25°C using the Clausius-Clapeyron equation. The activity data were in good agreement in the range 89-95% acid, but their overhauled accuracy was not better than 3%.

Tarasenkov (44) provided a smoothed set of experimental data on the vapour pressure of aqueous H_2SO_4 solutions between 5-85% acid and in the temperature range of 0-100%. The results were calculated and also provided in a graphical form. Deviations from the theoretical vapour pressure values were noticed at low temperatures and high acid concentrations.

Glueckauf and Kitt (45) required an accurate vapour pressure standard for an isopiestic determination of water activities of polystyrene sulphonate resins

at very low water activities. They selected sulphuric acid as their standard, and measured the vapour pressure at 25°C of sulphuric acid solutions containing 20-65 moles H_2SO_4 per 1000 grms. of water (66-86%). Free energy data, together with the heat contents and capacities measured by Kunzler and Giaque (39), permitted them to calculate partial thermodynamic quantities, which were tabulated for solutions up to 76 molal (88%). The method was tested by plotting $m_2 - m_1$ against m_1 for $m_1 < 10$ (where m_1 and m_2 were the molalities of the two sulphuric acid solutions), and comparing with a similar plot of Shankman and Gordon's (21) values.

Their observed values were found to differ by a constant amount of 0.08. The same difference was also found if the vapour pressure of 27.75 molal (73%) sulphuric acid of Hornung and Giaque (38) was used. They were unable to account for this small discrepancy and decide to add a correction of 0.08 to all their data for $m_2 - m_1$, making them agree perfectly with the data of both Hornung and Giaque (38) and of Shankman and Gordon (21), in the range of experimental observation.

procedure. Beyond 30 molal (75%), even though

independent isopiestic determinations deviate by

more than 1%, it is suggested that the smoothed

data do not lead to errors of more than 1% in

activity. Between 60 and 70 molal (85-87%), there

is no significant difference between their values

and those of Deno and Taft (42), although the

latter's values were not given to an accuracy of

better than 3%. Compared with the values listed

in the International Critical Tables, the water

activity differed by as much as 30% in the region

of $m = 60$ (85%).

One further paper by the Russian Uapakova

(46) appeared in 1957. He was able to determine

the sulphuric acid and water vapour partial pressures

in the 75-90% H_2SO_4 concentration range and from

100-180°C. It is of importance to note here that

the partial pressures of the water and sulphuric

acid for 91.15% H_2SO_4 at 140°C are 12.03 and 0.089

mm.Hg. respectively. Expressing the sulphuric

acid pressure as a percentage of the water vapour

pressure, then the value is 0.74%.

3. Materials

In the following work, an attempt has been made to confirm previous values for the water vapour pressures over sulphuric acid solutions at 25°C. In addition, the concentration has been extended up to 95% acid by direct measurements. Extrapolation of the obtained vapour pressure values has enabled this range to be extended up to 100% sulphuric acid. The well established gas saturation method has been employed in obtaining these results. Above 60% acid, the solutions were prepared with tritiated water, allowing a radioactive tracer technique to be introduced.

alcohol and ether were used for every 10 g. of borax crystals. After washing with alcohol and ether the borax was spread in a thin layer on a large watch glass and allowed to stand at room temperature for 16-24 hours. The borax was then dry and could be kept in a sealed tube for 2-3 weeks without any appreciable change in composition.

An alternative method of drying was to place

EXPERIMENTAL WORKA. Materials

Borax:- B.D.H. borax of analar grade was treated as recommended by Vogel (47). The analar borax was recrystallised from distilled water, 50 ml. of water being used for every 15 g. of borax. Care was taken to ensure that the crystallisation did not take place above 55°C - above which temperature there is a possibility of the formation of the pentahydrate since the transition temperature, decahydrate \rightleftharpoons pentahydrate is 61°C . The crystals were filtered at the pump, washed twice with distilled water, then twice with portions of ether. Five -ml. portions of distilled water, alcohol and ether were used for every 10 g. of borax crystals. After washing with alcohol and ether the borax was spread in a thin layer on a large watch glass and allowed to stand at room temperature for 18-24 hours. The borax was then dry and could be kept in a sealed tube for 2-3 weeks without any appreciable change in composition.

An alternative method of drying was to place

the recrystallised product (after having been washed twice with distilled water) in a desiccator over a solution saturated with respect to sucrose and sodium chloride. The borax is dry after about three days and may be kept indefinitely in the desiccator without any change. This latter method produces a material identical with that obtained by the alcohol-ether process but is more time consuming. The recrystallisation procedure was carried out three times before the borax was considered to be of the required standard.

Tests for the purity of the borax were carried out as recommended by Kolthoff and Stenger (48). The theoretical water content of borax is 47.22%. The water content was determined by drying a weighed quantity in a platinum crucible on a steam bath, at about 200°C and finally in an electric muffle at 700-800°C. The last molecule of water is difficult to drive off.

Provided the borax has been prepared properly and kept in a hygostat, the water determination is not essential.

Water:- Carefully prepared distilled water was allowed to run slowly through an ion exchange column. The

The smaller salt was readily purified by

column was packed with Amberlite Monobed Resin, MB. The conductivity water was then used in diluting the concentrated sulphuric acid in the preparation of acid solutions of desired strength. Freshly prepared water was used for every dilution.

Sulphuric acid:- The sulphuric acid was B.D.H. analar grade and was distilled under vacuum in an all glass apparatus. The first and last fractions of the distillate were rejected. The prepared acid solutions were stored in ground glass stoppered bottles, which had been used for storing sulphuric acid solutions previously. They were sealed off from the atmosphere by fitting a rubber gasket and using a 50 ml. beaker as a cap. No appreciable change in concentration was detected even after storage periods of six months.

Potassium Hydrogen Phthalate

The analar B.D.H. salt was dried in an oven at 120°C for two hours and then allowed to cool in a desiccator.

Potassium Iodate

The analar salt was readily purified by

recrystallising from distilled water and dried at 180°C for two hours. The recrystallising procedure was repeated.

Sodium Hydroxide Solution

The B.D.H. 1.0N solution was used and standardised against 1.0N HCl, which in turn was referred to potassium iodate as standard.

Typical titration figures were:

	24.98)	
25 ml. 0.9990 N HCl required	24.97)	24.98 ml. NaOH
	24.98)	
	24.98)	

solid dissolved. Each solution was titrated with

Therefore NaOH solution was 0.9998 N.

sodium hydroxide solution using phenol phthalein as

Hydrochloric Acid Solution

The B.D.H. N solution was standardised against potassium iodate solution using sodium thiosulphate conical flask and diluted with distilled water to 25 ml. and starch.

The solution was titrated with the 0.9998 N NaOH using

Typical titration figures were:

	39.84)	
25 ml. 0.1592 N KIO_3	39.83)	29.84 ml. HCl
	39.84)	
required	39.84)	

Therefore HCl solution was 0.9990 N.

B. Standardisation of Acid Solutions

deviation of 0.02% from the mean.

(1) Potassium Hydrogen Phthalate Standard

(a) Potassium Hydrogen Phthalate Standard

This salt is ideal as a standard as it has a high molecular weight, is not hygroscopic, and so can be weighed in an open container without danger of change.

standardised against the N NaOH solution using

screened Four 4-5 g. portions of the salt were

accurately weighed out into conical flasks, 75 ml. of boiled-out distilled water were added to each portion, each flask being stoppered and shaken gently until the solid dissolved. Each solution was titrated with sodium hydroxide solution using phenol phthalein as the indicator. Sufficient sulphuric acid to give a 25 ml. titration of the standardised sodium hydroxide solution was weighed from a weight-pipette into a conical flask and diluted with distilled water to 25 ml. The solution was titrated with the N NaOH using screened methyl orange as the indicator. A typical analysis gave:

65.55 65.63 65.62 65.53 % acid.

distilled water. Six portions of 0.4 to 0.5 g. were

The average value was 65.58% acid with a maximum deviation of 0.05% from the mean.

(2) Potassium Iodate Standard

The N HCl solution was first standardised against the KIO_3 solution using sodium thio-sulphate and starch. The N NaOH solution was then standardised against the N HCl solution using screened methyl orange as the indicator. Finally, using the same procedure as above, the sulphuric acid was standardised against the N NaOH using screened methyl orange as indicator. A typical analysis gave:

65.61 65.61 65.56 65.58 % acid.

The average value was 65.59% acid with the maximum deviation of 0.03% from the mean.

(3) The Borax Standard

Two N/10 sulphuric acid solutions were prepared by transferring appropriate volumes of the original acid into separate calibrated volumetric flasks. These were then made up to 250 ml. with distilled water. Six portions of 0.4 to 0.5 g. borax

were accurately weighed into corresponding flasks, dissolved in about 50 ml. of distilled water and then titrated with the acid solutions using methyl red as the indicator. The equivalent point was detected by comparison with a colour standard. The colour standard was prepared by adding five drops of methyl red to a solution containing 1.0 g. of sodium chloride and 22 g. of boric acid in 500 ml. of boiled-out water (47).

It is felt that the borax method, while not of the accuracy of Kusler's (46) method (1.01%) is at least as accurate as the iodate method analysis (10.01%) carried out by Shanklin and Gordon (1). A typical analysis gave:

65.58 65.60 65.57 65.58 65.59 65.61 % acid.

The average value was 65.59% acid with the maximum deviation of 0.02% from the mean.

Of the three methods employed in the analysis, it was found that the borax and iodate methods gave the more internally consistent results, and so these two methods were employed throughout. The borax method has been recommended by several investigators (49-57). Borax is stable under the proper storage conditions, has a high molecular and equivalent weight and does not absorb moisture during weighings. The

G. Calibration of Apparatus

standardisation of the acid may be carried out very quickly and simply. Thus it was decided that the borax would be used as a primary standard and the iodate method used as a cross-check whenever necessary. The 17 g. weight was taken as the

standard. The other pieces were then expressed in terms of this relative standard, by using the method of swings on a balance of known sensitivity and employing a subsidiary set of weights. The analysis ($\pm 0.03\%$) carried out by Shankman and Gordon (21).

It is felt that the borax method, while not of the accuracy of Kunzler's (40) method ($\pm 4.01\%$) is at least as accurate as the sodium carbonate analysis ($\pm 0.03\%$) carried out by Shankman and Gordon (21). The absolute values of the other weights were then readily calculated. All subsequent weighings were reduced to the true weight (weight in vacuo) by using the relationship (58)

$$W_v = W_a + \frac{\rho_a}{\rho_w} \left(\frac{W_a}{\rho_b} - \frac{W_v}{\rho_a} \right)$$

where

W_v = weight in vacuo

W_a = apparent weight in air

ρ_a = density of air

ρ_w = density of weights

ρ_b = density of body.

The difference between W_v and W_a does not usually exceed one or two parts per thousand and

C. Calibration of Apparatus

(1) Weights

A set of brass weights was used in all weighings. The 10 g. weight was taken as the standard. The other pieces were then expressed in terms of this relative standard, by using the method of swings on a balance of known sensitivity and employing a subsidiary set of weights. The absolute value of the relative standard was determined by comparison with a similar standard which had been calibrated at the National Physical Laboratory (N.P.L.). The absolute values of the other weights were then readily calculated. All subsequent weighings were reduced to the true weight (weight in vacuo) by using the relationship (58)

$$W_v = W_a + d_a \left(\frac{W_v}{d_b} - \frac{W_a}{d_w} \right)$$

where W_v = weight in vacuo

W_a = apparent weight in air

d_a = density of air

d_w = density of weights

d_b = density of body.

The difference between W_v and W_a does not usually exceed one to two parts per thousand and hence the expression may be reduced to

$$W_v = W_a + k W_a / 1,000$$

where $k = 1.20 \left(\frac{1}{d_b} - \frac{1}{8.4} \right)$

(2) Glassware

The glassware was limited to pipettes, burettes and volumetric flasks. Grade A flasks and burettes were used. Before use, the apparatus was thoroughly cleaned in fresh chromic acid, washed with distilled water and acetone, then carefully dried. Wherever possible, the glassware was handled with chamois leather and the calibration procedure adopted was that of Kolthoff and Stenger (59).

The aspirators were calibrated by weighing empty and then filled up to the two separate marks on the narrow neck, the temperature being recorded and the necessary corrections applied.

(3) Thermometers

Thermometers were only used at a temperature

of 25°C and were checked at this temperature by comparison with an N.P.L. thermometer.

Difficulties had been experienced by previous workers in measuring accurately the volume of air passed through the system. Thomas and Massey (7), after removing the vapour from the air stream, collected it by displacement of water from a calibrated vessel. Foote and Scholes (8) used a "wet gas meter" and claimed an accuracy of 0.1%. Derby, Daniels and Jutachs (9) designed an apparatus which consisted of two calibrated bulbs connected in series through three-way cocks with two eight litre bottles. The aspiration thus became a continuous process independent of the size of aspirating bottles. Unfortunately, the system was not too cumbersome to immerse in a thermostat, used air as the effluent gas, and was designed for very high flow rates (~24 l/hr.)

Pearce and Sore (11) generated their gas electrolytically and were able to calculate the volume passed through their solution very accurately. The simple displacement of air by running in water from a constant head arrangement was used by Bolton, Denbigh

D. Description of Apparatus

Difficulties had been experienced by previous workers in measuring accurately the volume of air passed through the system. Thomas and Ramsay (7), after removing the vapours from the air stream, collected it by displacement of water from a calibrated vessel. Foote and Scholes (8) used a "wet gas meter" and claimed an accuracy of 0.1%. Derby, Daniels and Gutsche (60) designed an aspirator which consisted of two calibrated bulbs connected interchangeably through three-way cocks with two eight litre bottles. The aspiration thus became a continuous process independent of the size of aspirating bottles. Unfortunately, the system was much too cumbersome to immerse in a thermostat, used air as the effluent gas, and was designed for very high flow rates (~ 24 L/hr.)

Pearce and Snow (51) generated their gas electrolytically and were able to calculate the volume passed through their solution very accurately. The simple displacement of air by running in water from a constant head arrangement was used by Balson, Denbigh

culated through a copper spiral, as observed in a
and Adam (52). It is of interest to note that in
thermostat, before entering the constant head and
their studies of the vapour pressure of mustard gas,
using the aspirator. The temperature was noted in
the consistency was better with the dynamic than
the constant head and the rate of flow of water
with the static measurements.

connected to a sink, thus allowing the water to
obtain a low Douglas (63), while measuring the vapour

pressure of methyl sulphoxide, collected the air
Variations in the water main pressure
in two bulbs which had previously been evacuated.
made it necessary to install a reservoir (30) well
On determining the final pressure in the bulbs the
above the constant head, thus ensuring a supply of
volume of air passed through the apparatus was then
water at a controlled rate of flow. A set of glass
calculated.

sets were prepared and roughly calibrated giving a

The air displacement arrangement of Balson,
Denbigh and Adam (52) seemed an accurate and simple
method of aspiration, and this technique was
adopted. These investigations measured the tem-
perature of the water on entering the constant head.

The more accurate method of total immersion of the
aspirator in a thermostat maintained at 25°C was
adopted in this work (Fig. 3). The calculation
to ensure that the pressure within the
of the water vapour pressure requires that the air
aspirator remained constant, i.e. the inflow of water
or nitrogen stream leaving the aspirator is saturated
was equal to the outflow of nitrogen gas, the water
with respect to water at 25°C. To ensure that
manometer was attached to the aspirator, the dif-
these conditions were attained, the water was cir-
ference in levels not exceeding one inch throughout

culated through a copper spiral. (A) immersed in a thermostat, before entering the constant head and hence the aspirator. The temperature was noted in the constant head B and the rate of flow of water was adjusted to a minimum, thus allowing the water to attain a temperature of 25°C .

Variations in the water mains pressure made it necessary to install a reservoir (~5L) well above the constant head, thus ensuring a supply of water at a controlled rate of flow. A set of glass jets were prepared and roughly calibrated giving a range of flow rates from 0.5-3 litres per hour. It was assumed that the flow rate necessary to obtain complete saturation of the nitrogen stream would be less than 3L/hr. This arrangement was found to work very satisfactorily and after the initial setting needed no supervision throughout the duration of the run.

To ensure that the pressure within the aspirator remained constant, i.e. the inflow of water was equal to the outflow of nitrogen gas, the water manometer W was attached to the aspirator, the difference in levels not exceeding one inch throughout

the run. The water jet (J) was detachable from the of the moisture. It could be renewed quite easily by constant head arrangement and could be substituted as simply heating for a few hours at 120°C; its colour required. change, blue to pink, was a self-indication for renewal.

The nitrogen stream leaving the aspirator was saturated with respect to water vapour and hence it is necessary to ensure the complete removal of this vapour before entering the saturators. A reference to the literature (64) showed that phosphorus pentoxide would serve the purpose admirably, as the weight of water vapour remaining in the gas stream after drying at room temperature was less than 2×10^{-5} mg/L. Initial trials, however, showed that the pentoxide tended to block the passage of the nitrogen gas after allowing relatively small volumes to pass through. Silica gel was installed as a preliminary drying agent to remove the bulk of the moisture and the pentoxide trap then functioned satisfactorily. The life of the trap was still very limited and the pentoxide itself very difficult to remove after use. Thus it was decided to introduce a liquid-air trap (S_1) whereby the weight of water escaping would be less than 2×10^{-23} mg/L (64). The silica gel tube (D) was still employed in removing the bulk of their vapour pressure studies of mustard gas. Essentially,

it was a horizontal coil of 10 mm. bore glass tubing of the moisture. It could be renewed quite easily by simply heating for a few hours at 120°C ; its colour change, blue to pink, was a self-indication for renewal.

The nitrogen stream, after leaving the liquid-air trap (S_1), was allowed to warm up to room temperature by circulating through another spiral (S_2). A mercury U tube manometer (H) was installed in the line at this stage enabling the pressure in the system to be observed. Large fluctuations in pressure during a run could thus be detected and the run discarded. The nitrogen gas was further circulated through spiral S_3 which was completely immersed in the thermostat enabling the gas to attain a temperature of 25°C before entering the saturator.

Vapour pressure studies of sulphuric acid solution have revealed the tendency of the acid to be carried over in the form of spray (7), (14). This tendency is always observed where a bubble-type saturator is used in a flow system. It was thus decided to select a non-bubble type saturator for this work. Such a saturator was used by Balson, Denbigh and Adam (62) in their vapour pressure studies of mustard gas. Essentially,

it was a horizontal coil of 10 mm. bore glass tubing in a compact flat spiral, giving a surface of about 150 sq.cm. for evaporation.

Initial experimental runs carried out in the lower acid concentration range (45-60%) with this saturator, yielded results which were very low when compared with those of Shankman and Gordon (21). It was presumed that saturation was not taking place and so the nitrogen flow-rate was reduced from 3L/hr. to 0.5L/hr. This led to an increase in the vapour pressure values but they remained inconsistent and only reached approximately 85% of the reported values. Saturation was obviously not occurring and hence a presaturator, identical in form to the saturator, was introduced into the line. This again resulted in an increase of the vapour pressure values but they remained inconsistent and fell short of Shankman and Gordon's (21) results.

It seemed that saturation would only occur if the flow rate was further decreased to a figure of probably 0.1L/hr. The duration of the run would then be 100 hrs. thus introducing further problems on flow-rate control and regular pressure measurements. The volume capacity of presaturator and saturator was

approximately 130 ml. Radioactive tracer techniques, to be introduced at a later date, required the usage of small quantities of acid solutions. Further experimental runs with this type of saturator were therefore abandoned.

A search through the literature (7), (13), (15), (46) revealed that the large capacity bubble-type saturator had been used in all vapour pressure determinations of sulphuric acid solutions by the gas saturation method.

Assuming a reasonable flow rate of 0.5-2L/hr. the rate of saturation will depend upon (a) intimate contact between the nitrogen gas and the acid solution, (b) the length of time during which the nitrogen remains in contact with the acid solution. Condition (a) is realised if the nitrogen gas is bubbled through the acid solution while (b) is not realised unless the gas is bubbled through very slowly or recirculated.

Condition (a) may be partially fulfilled by agitation of the solution. Mechanical rocking of the saturator achieves this purpose and was employed by Derby, Daniels and Gutsche (60). They constructed two

spherical saturators which were slowly rotated about a horizontal axis. The spheres were filled with glass beads and the solution being studied. The saturators were claimed to be extremely efficient even with flow rates of $\sim 20\text{L/hr}$. Agitation-type saturators still rely on a large working volume of solution and thus this method was rejected.

Redeman, Chaikin and Fearing (65) in their vapour pressure studies of cycloalkyl sulphides described a saturator which fulfilled conditions (a) and (b). A modified form of this saturator was eventually used in this work. Fundamentally, it is a bubble-type saturator (Fig. 2) with a small capacity, being designed for measurements on a very small quantity of liquid. The dry nitrogen enters at the point G (Fig. 2) and then bubbles through the coarsely sintered disc (A). The indentations (F) serve to agitate the acid solution thus increasing the efficiency of the saturation process. Small quantities of the acid solution are circulated upwards through the inner spiral by the nitrogen gas. Conditions (a) and (b) are thus being attained simultaneously. The bulb D breaks the acid-nitrogen bubbles, allowing the acid to return down through the outer wider spiral,

its weight be minimized. It has two hollow ground taps

the nitrogen taking the same path and thus remaining in contact with the acid solution. The process is a continuous one with "fresh" acid solution being exposed to the incoming nitrogen stream. Two traps (E) were built into the saturator to eliminate the possibility of water and sulphuric acid being carried over in the form of spray. It was found that the saturator functioned efficiently if the inner and outer spiral bores were 3.5-4 mm. and 8-9 mm. respectively.

A water pump was used for drawing the nitrogen gas through the line, resulting in a pressure gradient along the line. Calculation of the vapour pressure requires that the pressure within the saturator be known. An extended B10 cone joint was installed at C (Fig. 2) allowing a simple U-type mercury manometer to be attached, and the pressure difference recorded. The acid solution was introduced to the saturator from a 10 ml. pipette via this cone joint.

Saturated with respect to sulphuric acid and water, the nitrogen is passed into the liquid air trap S_4 (Fig. 3). This trap (Fig. 4) is a spiral constructed out of thin walled glass tubing in order that its weight be minimised. It has two hollow ground taps

T_3 and T_4 and may be suspended from a balance by nichrome wire. The trap was attached to the line by B10 cone joints. To ensure the complete removal of vacuum grease before weighing, B10 air leak type cones were used.

The nitrogen leaving the trap (S_4) is then bubbled through concentrated sulphuric acid contained in the Buchner flask (E). The acid served the dual purpose of (a) enabling observation of the flow rate of the nitrogen and (b) avoiding any creep back of moisture from the water pump. Early experimental runs revealed fluctuation in the water mains pressure resulting in variable flow rates. To compensate for this, a 5L aspirator (F) and a mercury cut-off valve was introduced between the water pump and the Buchner. The mercury valve was essentially the same as that of Balson, Denbigh and Adam (62) and maintained an approximately constant pressure. Large fluctuations in mains pressure showed that this arrangement was not quite adequate. It was later replaced by the manostat M (Fig. 5) which is a modification of the apparatus designed by Wade and Merriman (90).

Water pump suction, resulting in a decrease in

pressure starts circulation of the mercury in the direction indicated (Fig. 5). The side arm attachments (A) allow a pressure drop (below atmosphere) of 50-100 mm. Hg to be obtained. If the pressure suddenly increases, the mercury in the side arm (B) rises and in turn drops in the capillary (C), thus allowing more air to enter the system. The reverse procedure occurs when the pressure suddenly decreases, the mercury then rising in the capillary and sealing off the air inlet. This arrangement was found to work satisfactorily and maintained a pressure constant to within 0.2mm.Hg. Continual contact with the rubber connections during operation results in contamination of the mercury. Prior treatment of the rubber with dilute sodium hydroxide solution retards this action, thus allowing an extended period of operation.

Proving runs in the lower acid concentration range (45-60%) yielded results which were surprisingly high. The formation and carrying over of spray would account for such results. Attempts to eliminate this by introducing a trap of glass wool between saturator and the detachable weighing spiral (S_4) were unsuccessful. Complete immersion of the glass wool trap in the thermostat

still yielded high results. It was found that the difficulty could only be overcome by reducing the flow rate of nitrogen to 1-1.5 L/hr.

Removal of water vapour during a run was quite likely to result in a change of concentration of the acid solution. To avoid this it was decided to employ a presaturator (Fig. 1), essentially of the same form as the saturator but without the coarsely sintered disc. It was filled with approximately 6 ml. of the same acid solution as in the saturator and maintained at the same temperature (25°C).

Calculation of the vapor pressure required that the nitrogen leaving the saturator be saturated with respect to water vapour at 25°C . Nitrogen was passed into the aspirator for a period of 15 minutes with a known volume of water at 25°C above, the pressure of the nitrogen being continued for a further half hour. The apparatus was then left overnight to allow equilibrium.

The weighing tray was cleaned in alcohol and washed thoroughly with the distilled water.

E. Experimental Procedure

Appropriate quantities of the acid solution were transferred to the saturator (6.5 ml.) and pre-saturator (6 ml.) with a 10 ml. pipette, the tip of which had been cut off in order that rapid draining would occur. The B10 joints had already been greased with Edwards high-vacuum grease M, thus allowing immediate attachment of the saturators to the line. The U-type mercury manometer was attached to the saturator, the system then being left overnight in order that thermal equilibrium be obtained.

Calculation of the vapour pressure requires that the nitrogen leaving the aspirator be saturated with respect to water vapour at 25°C. Nitrogen was passed into the aspirator for a period of one hour and then a known volume of water at 25°C was added, the passage of the nitrogen being continued for a further half hour. The apparatus was then left overnight to attain equilibrium.

The weighing trap was cleaned in chromic acid, washed thoroughly with the distilled water and allowed to

dry at 110°C . Careful greasing of the hollow ground taps was followed by the fitting of the nichrome wire. The trap was washed thoroughly with ether and transferred to the balance, chamois leather being used throughout. In determining the weight, an identical spiral trap was used as a counterbalance.

Prior to the actual run, nitrogen was introduced to the line and bubbled through the saturators for about half an hour. Attachment of the weighed trap, followed by the connection of the line to the aspirator, left the system ready for operation. The manostat was adjusted in the first few minutes of the run, allowing atmospheric pressure to be maintained in the aspirator.

Readings of barometric pressure (P), temperature (t) and manometric pressure in the saturator (p_m) were taken every 30 minutes or 60 minutes depending on the duration of the run. Constant checking of the temperature of the thermostats and water inlet were also made. The run time was recorded in order that the flow rate could be estimated. Severe atmospheric pressure changes were found to affect the results: runs carried

out under such conditions were rejected. Mains water pressure fluctuations were found to affect the results in a similar manner.

The weighed trap S_4 (Fig. 4) was cooled with liquid air during a run and hence when allowed to warm up to room temperature, developed a pressure considerably greater than atmospheric. To equalise these pressures, it was found necessary to "crash-warm", i.e. warm the trap up to room temperature rapidly by washing with distilled water. Trial experiments with similar weighed traps containing small quantities of water proved that no loss in weight occurred during this process.

After crash warming, and careful removal of all traces of grease with cotton wool and ether, the whole trap was washed with distilled water and ether, transferred to the balance room with chamois leather, and weighed to constant weight.

Fresh acid solutions were introduced to the saturators for every run, although successive runs on the same acid solutions produced identical results. The acid solution removed from the saturator at the end of a run was analysed by the borax method as previously described.

RESULTS

The formula used for calculating the vapour pressure is essentially the same as that employed by Tamman (66), except that it was found unnecessary to introduce any correction for change of volume of the aspirator, since it was calibrated and used at the one temperature, namely 25°C. The symbols employed and their significance together with the numerical constants used in developing the formula are as follows:

P = Barometric pressure in inches.

t = Balance room temperature in °C.

P_c = Barometric pressure corrected for scale temperature, latitude and sea level in mm.Hg.

P_m = Manometer reading attached to the saturator in mm.Hg.

P_w = Partial pressure of water vapour.

P_s = Partial pressure of sulphuric acid.

P_n = Partial pressure of nitrogen.

V_1 = Volume of aspirator at 25°C.

V_2 = Volume of nitrogen and water vapour passing through saturator.

p_w^0 = Vapour pressure of water at 25°C =

Substituting $23.779 \text{ mm.Hg. (96)}$

w = Corrected weight of water vapour determined by weighing.

W = Molecular weight of water = 18.016.

w_n = Weight of nitrogen aspirated.

N = Molecular weight of nitrogen = 28.016.

Considering the nitrogen in the aspirator
Assuming Dalton's law of partial pressures

$$P_c - P_m = P_w + P_s + P_n \dots\dots\dots(a)$$

The partial pressure of sulphuric acid may be considered to be zero, and so (a) is reduced to

$$P_c - P_m = P_w + P_n \dots\dots\dots(b)$$

Considering the water vapour and nitrogen and applying the gas laws, then

$$P_w V_2 = \frac{w}{W} \frac{RT}{273.15}$$

and $P_n V_2 = \frac{w_n}{N} \frac{RT}{273.15}$

Eliminating V_2

$$P_n = \frac{w_n W}{w N} P_w$$

Substituting this value of P_n in (b) we obtain

$$P_c - p_m = p_w \left(1 + \frac{W w_n}{N w} \right) \dots \dots \dots (c)$$

Substituting this value in (a)

$$P_c - p_m = p_w \left(1 + \frac{W w_n}{N w} \right) \dots \dots \dots (c)$$

The unknowns in this equation are p_w , which we wish to calculate, and w_n .

Considering the nitrogen in the aspirator and saturator and applying the gas laws

$$(P - p_w^0) V_1 = (P - p_w - p_m) V_2$$

$$\text{and so } V_2 = \frac{(P - p_w^0) V_1}{P - p_w - p_m}$$

Correcting this volume to N.T.P.

$$V_{N.T.P.} = \frac{273.18 V_1 (P - p_w^0)}{760 \times 298.18}$$

The results are given in tabulated form in the following pages. The symbol δ represents the individual vapour

As 22,402.9 ml. nitrogen at N.T.P. weigh 28.016 g. (97)

$$V_{N.T.P.} \text{ ml. weight } \frac{28.016 V_{N.T.P.}}{22,402.9} = w_n$$

Substituting this value of w_n in (c) we obtain

$$P_c - p_m = p_w \left(1 + \frac{W \cdot 28.016 \cdot V_{N.T.P.}}{22,402.9 \cdot N \cdot \omega} \right)$$

which reduces to

$$p_w = \frac{P_c - p_m}{1 + \frac{(P - p_w^0) \times 273.18 \times 18.016 \cdot V_1}{\omega \times 22,402.9 \times 760 \times 298.18}}$$

$$\text{The term } \frac{273.18 \times 18.016 \times V_1}{22,402.9 \times 760 \times 298.18}$$

for the majority of runs is a constant and hence

$$p_w = \frac{P_c - p_m}{1 + \left(\frac{P - 23.779}{\omega} \right) K}$$

Vapour pressure determinations on 45.68, 51.16, 56.08 and 60.97% acid were carried out initially. The results are given in tabulated form in the following pages. The symbol δ represents the individual vapour pressure deviation from the average vapour pressure value obtained from the dozen runs.

45.68% acid

Run Number	P	t	P _C	P _M	V ₁	w	P _W	δ
1	29.772	17.50	754.75	80.14	10,012	0.1130	10.576	+0.009
2	29.692	17.70	752.12	82.84	10,012	0.1130	10.530	-0.037
3	29.606	18.63	749.83	78.05	10,012	0.1126	10.565	-0.002
4	30.333	21.23	767.87	81.06	10,790	0.1214	10.548	-0.018
5	30.090	15.72	762.48	82.24	10,390	0.1175	10.576	+0.009
6	30.429	17.48	770.84	82.11	10,390	0.1174	10.581	+0.014
7	30.377	17.52	769.52	80.79	10,012	0.1130	10.587	+0.020
8	29.623	18.12	750.34	82.70	10,012	0.1135	10.576	+0.009
9	28.813	18.38	729.84	84.43	10,012	0.1140	10.561	-0.006
10	30.105	19.53	762.38	83.40	10,012	0.1136	10.592	+0.025
11	29.984	21.49	759.08	80.50	10,390	0.1169	10.544	-0.023
12	29.702	17.52	752.399	81.60	10,790	0.1220	10.569	+0.002

Average value of P_W = 10.567 mm.Hg.

51.16% acid

Run Number	P	t	P _c	P _m	V _l	w	P _w	δ
1	30.011	20.50	759.89	81.04	10,012	0.0826	7.759	-
2	30.397	22.05	769.49	81.50	10,012	0.0826	7.763	+0.004
3	30.462	21.80	771.09	74.81	10,012	0.0817	7.755	-0.004
4	29.823	18.82	755.37	80.80	10,790	0.0891	7.764	+0.005
5	29.241	19.23	740.56	81.50	10,012	0.0829	7.761	+0.002
6	30.213	22.50	764.819	83.90	10,012	0.0828	7.750	-0.009
7	30.040	19.38	760.83	80.66	10,012	0.0825	7.755	-0.004
8	29.126	18.62	737.72	82.81	10,012	0.0831	7.761	+0.002
9	30.165	15.70	764.36	83.28	10,790	0.0894	7.770	+0.011
10	29.670	21.04	751.15	82.55	10,012	0.0830	7.769	+0.010
11	30.066	21.17	761.24	80.80	10,790	0.0890	7.761	+0.002
12	29.268	17.83	741.40	83.86	10,012	0.0830	7.743	-0.016

Average value of P_w = 7.759 mm. Hg.

56.08% acid

Run Number	P	t	P _c	P _m	V _l	w	P _w	δ
1	30.546	21.35	773.33	87.96	10,012	0.0587	5.486	+0.013
2	30.377	20.90	769.09	84.02	10,790	.0628	5.474	+0.001
3	29.419	18.33	745.19	85.95	20,024	.1174	5.481	+0.008
4	29.594	17.68	749.61	85.92	20,024	.1172	5.475	+0.002
5	29.903	18.08	757.48	89.72	21,580	.1266	5.463	-0.010
6	30.095	20.24	762.10	83.73	20,024	.1165	5.470	-0.003
7	30.421	19.80	770.20	76.81	20,024	.1153	5.474	+0.001
8	30.595	19.49	774.80	76.93	20,024	.1153	5.476	+0.003
9	30.091	20.09	762.00	85.45	20,024	.1167	5.465	-0.008
10	30.368	21.45	768.81	83.20	20,024	.1164	5.474	+0.001
11	30.009	20.47	759.56	81.50	20,024	.1164	5.481	+0.008
12	29.826	21.03	755.14	82.70	20,024	.1252	5.458	-0.015

Average value of $p_w = 5.473$ mm.Hg.

60.97% acid

Run Number	P	t	P _C	P _m	V _l	w	P _w	δ
1	30.222	19.50	765.38	87.38	20,024	0.0748	3.50 ₅	-0.002
2	30.008	21.50	759.69	81.39	21,580	.0801	3.51 ₁	+0.004
3	30.037	19.49	760.71	81.53	20,024	.0.742	3.50 ₅	-0.002
4	29.951	20.08	758.44	85.09	20,024	.0745	3.49 ₉	-0.008
5	30.038	19.13	760.81	86.60	20,024	.0750	3.51 ₆	+0.009
6	29.955	18.37	758.80	83.04	20,024	.0746	3.51 ₅	+0.008
7	29.813	16.95	755.24	81.26	10,012	.0370	3.49 ₄	-0.013
8	30.165	18.62	764.01	82.77	20,024	.0744	3.50 ₉	+0.002
9	29.593	19.52	749.43	83.00	20,024	.0745	3.50 ₆	-0.001
10	30.333	20.47	767.99	82.10	21,580	.0799	3.50 ₂	-0.005
11	30.200	19.51	764.82	82.60	20,024	.0744	3.50 ₉	+0.002
12	30.102	18.36	762.51	83.70	20,024	.0747	3.51 ₈	+0.011

Average value of P_w = 3.50₇ mm.Hg.

Radioactive Work

A radioactive tracer technique for the determination of the vapour pressure of white phosphorus by a static

A. General Introduction based on "counting" a given volume of vapour at a fixed temperature in equilibrium

Radioactive elements produce ionization by their radiations, thus providing a means of measuring minute quantities of such elements. Properties which are outside the sensitivity of ordinary methods of measurement can be determined for compounds of such elements. Young, Goodman and Kovitz (67) made use of this natural phenomenon as far back as 1939 when they considered those elements, occurring in the thorium and uranium series, which emitted α -particles. Solubility and vapour pressure measurements were made on thorium acetylacetonate. The vapour pressure was determined as 3.2×10^{-4} mm. at 100°C by saturating a slow stream of nitrogen with thorium acetyl acetone vapour, which was decomposed by passing into alcoholic hydrochloric acid. The α -activity of the scrubber was determined, and from the known volume of nitrogen and the α -activity of a known weight of thorium, the vapour pressure was estimated from the gas laws.

More recently, Dainton and Kimberley (68) employed

a radioactive tracer technique for the determination of the vapour pressure of white phosphorus by a static method. The method was based on "counting" a given volume of vapour at a fixed temperature in equilibrium with a sample of the condensed phase at a lower temperature, the latter being labelled with the radioactive isotope p^{32} .

The measurement of the vapour pressure of sulphuric acid solutions by the air saturation method is theoretically possible over the whole acid concentration range. After passing ten litres of nitrogen through 45% acid the moisture trapped out weighs approximately 0.12 g. This quantity can be determined to within ± 0.1 mg. thus representing a weighing error of $\pm 0.1\%$. When the acid concentration has been raised to 60% acid the weight of moisture trapped falls to 0.04 g. with an error of $\pm 0.3\%$. Further increase in acid concentration to 70% acid results in a weighable quantity of 0.01 g. with the corresponding error of $\pm 1\%$.

It is apparent that the vapour pressure of the acid solution cannot be measured over the complete acid range unless some other method of determining the moisture

It has not, however, been extensively used is available. If the acid solution was made up with a tracer in the water content then it would be possible to "count" the water rather than weigh it. The activity could be introduced via either the oxygen atom or the hydrogen atoms. Of the six isotopes of oxygen, three of these are non-emitters and the other three (atomic mass of 14, 15 and 19) emit γ and β type radiation. Unfortunately, the half-lives of these latter three range from 29.4 to 119 seconds thus making them unacceptable for the present work. Hydrogen has three isotopes of atomic mass 1, 2 and 3. Tritium is the only emitter of the three.

Tritium is made by the bombardment of lithium with neutrons



The gas obtained emits beta particles of very low energy (Max. 0.015 Mev), has a moderately long half-life of 12.26 years and the very high specific activity of 2.7 curies/standard ml. This isotope is relatively cheap to produce and because of its low energy of radiation quite safe to handle and hence would appear to be very useful for many research problems.

It has not, however, been extensively used because beta particles of such low energy cannot be counted by the simple techniques which are applicable to, for example, C^{14} , which emits beta rays sufficiently energetic (0.155 Mev) to penetrate the window of an end-window counting tube. It is therefore usual to introduce the tritiated material into the body of the counter, a procedure which necessitates the use of a vacuum line, of greater or less complexity according to the nature of the filling mixture. More recently, scintillation counting, which simplifies the handling of the tritiated compounds, has gained favour. The counting efficiency of this method is, particularly in the case of tritium, lower than that of gas counting.

Water of very low tritium content has been assayed visually in a cloud chamber by Fireman (69) who was interested in the proportion of tritium in natural water.

The rapidity of exchange between hydrogen and tritium atoms is another difficulty encountered when handling tritiated compounds. Exchange between deuterium

and hydroxyl or amino hydrogen at room temperature is immeasurably fast, slow with hydrogen atoms activated by a keto group and slight with unactivated hydrogen. This subject has recently been reviewed by Kimball (70) and Satchell and Gold (71).

Surprisingly fast exchanges occur between tritium gas and organic compounds, even when the latter contain no activating groups (72). It follows that the interpretation of results of experiments involving tritium will be seriously affected unless every precaution is taken to exclude or allow for these exchange reactions. Contamination of glassware and exchange with atmospheric water vapour are potential sources of error, particularly if small quantities are manipulated.



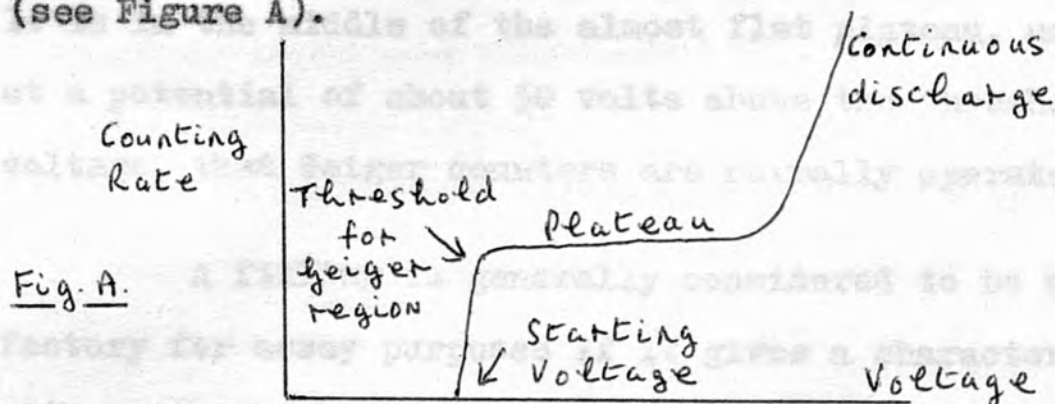
In practice, it is usual to

best operating potential by

B. Gas Counting of Tritium

The great variety of published methods of tritium assay suggests that none of them is entirely satisfactory. Although the electronic equipment used by different workers is far from standard, the main difference between these methods is in the form in which the tritiated material is introduced into the Geiger-Müller counting tube.

The performance of the tube is dependent on, amongst other things, the nature of the filling gases, a "good" filling being one which gives both a low starting voltage, and a long plateau with a low slope (see Figure A).



In practice, it is usual to determine the best operating potential by increasing the positive

voltage on the central wire from zero and observing the rate of counting obtained from a source of constant activity. Below a certain voltage, in the region where the counter is operating as an ion chamber, the pulse height is in general too small to operate the recording apparatus. As the proportional region is reached with rise of potential, the pulse amplitude increases and at a certain starting potential becomes large enough for counting to commence. As the potential is further raised the counting rate increases until the Geiger region is reached, in which the counting rate is almost independent of the applied potential. Eventually, the counting rate begins to rise rapidly and the counter breaks into continuous discharge. It is in the middle of the almost flat plateau, usually at a potential of about 50 volts above the threshold voltage, that Geiger counters are normally operated.

A filling is generally considered to be satisfactory for assay purposes if it gives a characteristic with a plateau at least 100 volts long and a slope of not more than 0.03% per volt. As the processes which

occur within the Geiger tube are not yet fully understood, the selection of the filling ingredients is still largely a matter of trial and error. The rare 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 the halogens are considered to be undesirable in a counter (73), because of their tendency to form negative ions sufficiently mobile to cause spurious pulses immediately after the electrons have been collected (74). This results in a marked increase of plateau slope and, frequently, total disappearance of the plateau.

Water vapour has approximately the same electron attachment coefficient as oxygen and for this reason was until recently rigorously excluded from counter fillings (75). The poor counting characteristics of water vapour are particularly unfortunate because in many physico-chemical problems the measurement of small quantities of water is fundamental. In biochemical tracer work, labelled organic compounds are

usually oxidised to CO_2 and water so that here too direct counting of tritiated water would be useful.

Direct water counting has been attempted by a few workers. Fontana (76) used a filling of 1 cm. pressure of water vapour and 2 cm. propane. Another group (77) claimed that provided the pressure of water vapour was kept below 2 mm., the counter characteristics were not affected. In order to compensate for the small amount of tritium which could be introduced into the counter tube, they used a specially constructed counter with a volume of one litre. The pressure of water introduced was measured by a high-reading McLeod gauge, 2.5 cm. of anhydrous alcohol and 2.0 cm. of argon were required to make up the filling. The mean standard error of this method was $\pm 3.7\%$. Neither of these papers included a full description of the counter characteristics.

In 1955, Cameron (78) stated that a tube containing 1 cm. of ethyl alcohol and 10 cm. argon (a standard filling with excellent counting properties) would tolerate a pressure of 1.5 cm. of water vapour

without any deterioration of the characteristics. He was not interested in tritium assay and so did not establish the method for this purpose. So far, (1959), no paper has been published in which this filling was used.

A filling consisting of helium saturated with water has been described by Bradley and Bush (79) who were seeking a simple means of tritium assay suitable for routine work in hospitals. Several general papers on aqueous fillings (80) suggest that even if an aqueous filling with a satisfactory Geiger characteristic was found, it would probably be unsuitable for tritium assay because of adsorption of the active water by glass or exchange with difficultly removable water molecules in the glass counter. Experiments with polythene or silicone counters were proposed as a solution to the first problem and would no doubt overcome the second effect.

Counter tubes are always highly contaminated by aqueous fillings; the count rate after pumping out in a high vacuum line for one hour may be as high as 20% of the initial count. This was held to be a

serious disadvantage until Cameron (78) showed that it could be reduced almost to normal by flushing several times with 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. It was developed by Joris and Taylor (81), who used 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 vapour 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 Geiger tube and argon added to give a standard 10:1 argon-alcohol ratio.

This filling has been used for many purposes and has been fully investigated by Spatz (82) who found that plateaus at least 400 volts long and having a slope less than 1% were obtained under appropriate conditions. This filling was used in the early part of the present investigation and characteristics even better than this were obtained. Plateaus 800 volts long with a slope of less than 0.3% were not uncommon.

Although the characteristics of this filling could scarcely be bettered, the method is not ideal for tritium assay. The ratio of argon to alcohol is critical, the plateau slope increasing very rapidly with increasing proportions of alcohol (82). The amount of tritiated vapour which can be introduced is therefore limited to between one and two cm. pressure, because optimum total pressure in an argon-filled counter is about 15 cm. Accurate measurement of the amount of alcohol added is therefore difficult. With an ordinary manometer an error of 2.5% may be expected. A second disadvantage is contamination of the tube, but this is no longer serious. (83). Alternatively, a Helium tube

can be used in conjunction with a proportional counter

(54). Geiger counting with various mixtures of hydrogen, ethanol, helium and argon has been described by Zisman (79). The filling consisted of helium saturated with tritiated acetone, and gave a plateau of slope 0.05% at 2,500 volts. This method has the advantage that all six hydrogen atoms of acetone exchange, so that for the same pressure of vapour acetone is six times as active as alcohol. It has the disadvantage of a longer exchange time, but as this exchange is very slow unless catalysed, the acetone will not contaminate the tube, nor will it lose activity during handling. The exchange time is probably much less than the time involved in those methods which depend on chemical conversion.

The more important techniques of class (b) were reviewed by Glasscock (75) in 1955. In these methods the water is converted either to hydrogen by reduction with zinc dust, magnesium amalgam or lithium aluminium hydride, or to a hydrocarbon by reaction with a carbide or Grignard reagent. Hydrogen is a poor counting gas and hence the use of an ionisation chamber as a detector is sometimes preferred (83). Alternatively, a Geiger tube can be used in conjunction with a proportional counter

(84). Geiger counting with various mixtures of hydrogen, ethanol, helium and argon has been described by Kamen (85), but as the only characteristic mentioned was a plateau length of 40 volts, these fillings do not seem to be very promising.

A more recent paper (86) gave details of a quench circuit, the use of which permitted Geiger counting of hydrogen gas at atmospheric pressure. The plateau began at 3,100 volts, which is remarkably low for such a high pressure filling, and had a slope of 0.01%. This would appear to be the most satisfactory method of hydrogen counting.

Hydrocarbons are much easier to handle than hydrogen because at liquid air temperature they are completely condensed and therefore more conveniently transferred from one section of the vacuum line to another. Acetylene (87), methane (88) and butane (89) have been used as counter fillings. The methane fillings showed no Geiger region, a fact which was attributed to impurities such as H, OH, S and NH. White (89) therefore conducted the methane counting in the proportional region where a plateau of 200 volts and slope 0.03% were

obtained.

Butane, which is completely condensed at liquid-air temperature, seems to be the only filling to have found favour amongst other workers. The Geiger characteristics are good, the plateau length being 800 volts and the slope 0.03%. The starting voltage at the optimum pressure of 14 cm. is 3,200 volts. This is rather high and electrical leakages across the terminals of the counter tube may occur, resulting in fluctuating count rates and occasionally a complete cessation of counting. Glascock recommends that the glass surrounding the electrodes be coated with a silicone polymer in order to prevent this.

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



An ethereal solution of butyl magnesium bromide is prepared from rigorously dried and purified reagents.

4. Selection of Assay Techniques for the Present Work

Portions of this solution are then transferred to reaction vessels, attached to the vacuum line and the ether pumped off. It is then necessary to "cook" the reagent under high vacuum for two hours at a temperature of 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 analysis due to the formation of inactive butene in the subsequent reaction with water. Fresh supplies of reagent must be prepared every week because "ageing" is also conducive to butene formation. The final process of reaction with water is conducted by heating for one hour at 120°C , the butane so formed being measured manometrically and condensed into a Geiger tube. The results obtained by Glascock were reproducible to within $\pm 2\%$.

The tritium atom is directly attached to the carbon atom and hence contamination in the normal sense does not occur, but solubility of the butane in vacuum grease was occasionally a source of error.

C. Selection of Assay Technique for the Present Work

The factors governing the choice of method were

- (a) the apparatus available.
- (b) the adaptability of the method to the measurement of microgram quantities of tritiated water.
- (c) reliability.
- (d) the speed and simplicity of assay.

The electronic equipment available was a Dynatron 4Kv power pack, an Ericsson deca-tron scaler, a probe unit and a pair of 20th Century GA/IOM gas counting tubes. Techniques requiring proportional counters or ionization chambers had therefore to be excluded. Considerations (b) and (d) suggest that the use of one of the direct methods would be the most logical. The reliability of these methods is, however, questionable.

The reliability of tritium counting techniques in general is difficult to assess because many of the publications do not give adequate 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. Glascock himself estimated that a full time assistant would be unable to assay more than 18 samples a week. Thus for a single-handed worker the time involved would be prohibitive. It was therefore decided that the reliability of the methods of Cameron (78), and Joris and Taylor (81) should be investigated and adapted to the present work.

Materials:-

Ordinary absolute alcohol as supplied by the Distillers Company was used throughout.

(i) Description and Operation of Apparatus

Initially, the active acid solutions were prepared by weighing out the tritiated water into a 100 ml. ground-glass stoppered flask, cooling with ice water, and careful addition of a predetermined quantity of sulphuric acid with a further weighing.

It was soon realized, and experimentally verified,

D. Experimental Section

in the water content were occurring in such processes, due to the heat of

(i) Materials

Tritiated water:-

This was obtained direct from Harwell and diluted with fresh conductivity water as required. The original quantity obtained was 0.2 g. with an activity of 0.2 curie.

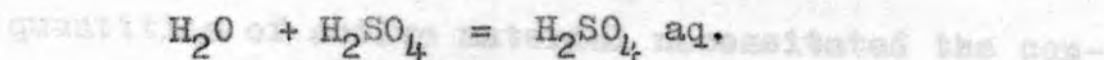
Alcohol:-

Ordinary absolute alcohol as supplied by the Distillers Company was used throughout.

(ii) Description and Operation of Apparatus

Initially, the active acid solutions were prepared by weighing out the tritiated water into a 100 ml. ground-glass stoppered flask, cooling with iced water, and careful addition of a predetermined quantity of sulphuric acid with a further weighing.

It was soon realised, and experimentally verified, that appreciable losses in the water content were occurring in such processes, due to the heat of reaction of



Preparation of the acid solution by distillation under vacuum was attempted, and rejected because of practical difficulties encountered in handling large quantities. Sufficient acid solution for ten vapour pressure determinations and an acid standardization was needed for each concentration of acid prepared.

It was decided to prepare the solutions by addition of weighed quantities of tritiated water to a known quantity of the concentrated acid. Water losses would occur but these could be calculated from the standardization figures. A blank was carried out at the same time in order to estimate the moisture picked up from the atmosphere during the preparation of the acid. A typical set of figures illustrating this procedure are given in the following results section.

Health hazard standards were maintained by ensuring that all work connected with active material was carried out in a fume cupboard.

The handling and manipulation of small quantities of active material necessitated the construction of a pyrex vacuum line. Evacuation was effected through a pair of liquid-air traps (fig. 6) by a two-stage Edwards high-vacuum pump. The pressure in the line was checked with an Edwards Pirani vacuum gauge having a range of 1×10^{-4} - 0.5 mm.Hg. After evacuation to less than 10^{-3} mm.Hg., the two-litres argon storage flask (A) was filled directly from a cylinder, the gas first being passed through a liquid-air trap. The B.10 joints (B and C) allowed the attachment of sample tubes or the spiral "weighing" trap at the close of a vapour pressure determination.

The Geiger gas counting tube (E) could be similarly attached for evacuation and filling. Pressure fillings were recorded on a mercury manometer (D) of 5 mm. bore tubing. Decontamination of the tube was carried out by attachment to a separate section of the line (F) and repeated flushing with

distilled water (G).

Active samples for initial experiments, were prepared by the addition of requisite quantities of alcohol to the stock solution of tritiated water (40;1 by volume). Samples were attached to the vacuum line and repeatedly pumped off (about a dozen times) at liquid-air temperature until all of the dissolved gases had been removed. After allowing the sample tube to warm up to room temperature, about 3 cm. pressure was introduced to the manometric chamber and eventually into the gas counter. A similar procedure was followed for the "topping-up" argon filling, care being taken to ensure that the argon:alcohol ratio was close to 10:1 (78). It was then necessary to allow some time to elapse (20-30 minutes), thereby enabling the gases to mix and achieve adsorption equilibrium before counting.

Five-minute counts were taken with increasing voltage (100 volts steps) until the plateau was established. If the filling showed good counting characteristics (plateau length \geq 200 volts and slope \leq 0.5% per volt), ten five-minute counts were taken at the centre of the plateau. The above method of filling gave plateaus

of 400-800 volts with slopes $< 0.2\%$ depending on the pressure filling. The characteristics of these fillings could scarcely be improved upon, but unfortunately the disadvantages are many.

The argon/alcohol ratio is critical, the plateau slope increasing rapidly with increasing proportions of alcohol. The maximum pressure filling is limited to 15 cm., thus restricting the tritiated vapour which could be introduced. Filling with the active alcohol is followed by evacuation and filling with the argon, thus introducing possible losses of active alcohol. Finally, the plot of counts per minute (c.p.m.) versus alcohol pressure filling does not follow a true linear relationship, thereby introducing errors in estimating the c.p.m. for a standard filling (3 cm. pressure of alcohol).

Dobson (92), while working on methods of assay of tritium, had noticed that direct filling of the counter with active alcohol (1-1.5 cm.) produced plateaus of more than 100 volts. Further work on this filling soon revealed that plateaus of 200-400 volts (with alcohol, not less than five samples being prepared. A

series of c.p.m. were then determined for a range of slopes of $< 0.2\%$ per volt) were easily obtained.

A plot of c.p.m. versus alcohol pressure filling gave an excellent linear relationship (see fig. 7). The plateau length and threshold voltage were found to increase with increase in pressure filling (see fig. 8) up to a maximum of 4.5 cm. alcohol. Beyond this, the efficiency of the counting diminished, probably due to the condensation of the alcohol in the Geiger tube.

The actual counting was carried out with the Geiger tube placed fully inside a cylindrical block lead castle ($2\frac{1}{2}$ inches thick). This was maintained at a temperature of 30°C ($\pm 0.5^{\circ}\text{C}$) by an electrically heated coil. Larger pressure fillings of the tube are probably possible provided the lead castle is maintained at a temperature sufficiently high to eliminate condensation.

It was necessary to "calibrate" the three stock solutions of tritiated water. This was carried out by weight dilutions with appropriate quantities of alcohol, not less than five samples being prepared. A

series of c.p.m. were then determined for a range of alcohol pressure fillings. The calibration plot of c.p.m. for a standard filling of 3 cm. alcohol versus water-to-alcohol weight ratio, was a straight line passing close to the origin. Three such plots were obtained (figs. 9-11) and equations fitted by the method of least squares.

High counts were obtained from these dilutions and difficulties were encountered in decontaminating the tubes. A tube was considered satisfactory for assay work if its background count could be reduced to 50 c.p.m. Effective decontamination could only be obtained by repeated flushing with distilled water (78), flaming of the tube while under high vacuum, and in several cases the severe treatment of boiling inactive water inside the tube. This last procedure is only recommended for extreme cases.

The vapour pressure runs with the active acid solutions were carried out in an identical manner to that used for the previous runs. The flow rate was reduced for the more concentrated, and hence more viscous acid solutions, thus ensuring complete saturation of the

nitrogen gas. It is of interest to note that above 85% acid (~ equimolar), excessive frothing of the acid occurred in the saturators during a run. To enable efficient operation of the saturator under such conditions, the working volume of acid was reduced to 5 ml.

Difficulties were experienced in introducing small quantities of alcohol into the moisture trap at the close of a run. These were overcome by a modification of the trap. A side arm with a B.10 stoppered joint was attached to the upper section of the spiral, the alcohol then being introduced from a weight-pipette prior to the commencement of a run. At the end of a run the trap was immediately attached to the vacuum line, repeatedly pumped off and allowed to equilibrate at room temperature.

Two hours were allowed to elapse before the alcohol was introduced into the Geiger tube. The counting procedure was identical to that used in the calibration of the stock solutions, i.e. confirmation of plateau and then a series of long counts in the middle of the plateau. The number of counts (N) recorded normally exceeded 100,000 thus reducing the mean deviation ($\Delta = \sqrt{N}$) to 0.31%.

The contamination of the saturators was considered to be a likely source of error. This was eliminated by continual washing with inactive water, followed by flushing on the vacuum line. The background sample, used for checking the decontamination process, was prepared by the addition of 40 ml. of alcohol to 1 ml. of conductivity water. It will not be the same as that of the free water present in the acid solution. It will be assumed that the composition of the water vapour carried over in a vapour pressure determination will be the same as that of the free water in the acid solution.

The two effects to be considered are (a) dilution due to the water present in the concentrated acid and (b) dilution due to the exchange of the tritium atom in the water molecule with the hydrogen atom in the sulphuric acid molecule. It is reasonable to assume that the processes (a) and (b) are directly proportional to the number of moles of water and sulphuric acid present in solution.

A typical set of figures illustrating this procedure are given:-

Active acid:-

Results

Weight of flask = 57.5054 g.

Weight of flask + acid = 69.3679

The specific activity of the tritiated water will alter in the preparation of the acid, i.e. the specific activity of the original stock solution will not be the same as that of the free water present in the acid solution. It will be assumed that the composition of the water vapour carried over in a vapour pressure determination will be the same as that of the free water in the acid solution.

Blank:-

The two effects to be considered are (a) dilution due to the water present in the concentrated acid and (b) dilution due to the exchange of the tritium atoms in the water molecule with the hydrogen atoms in the sulphuric acid molecule. It is reasonable to assume that the processes (a) and (b) are directly proportional to the number of moles of water and sulphuric acid present in solution.

A typical set of figures illustrating this procedure are given:-

Active acid:- acid present = 53.24×33.7446

Weight of flask = 67.5054 g.

Weight of flask + acid = 69.3679

Weight of flask + acid
+ tritiated water = 101.2500

Weight of acid = 28.8625

and Weight of water = 4.8821

and active water weighed out = $4.8821 - 0.0012$
Total weight = 33.7446
= 4.8809 g.

Time of operation = 3 minutes.

(a) effect of water dilution

Blank:-

Weight of flask = 76.4396 g. stock

Weight of flask + acid = 104.9143 g.

Weight of flask + acid
after 3 minutes = 104.9155 reduced by

a factor moisture picked up = 0.0012 g.

Standardization figures revealed that the
solution was 85.24% acid, hence

Total water present = 4.9807 g.

Total acid present = 28.7639 g.

Total acid present = 85.24×33.7446

Hence the specific activity 100 will be reduced by

a factor, f_2 , where

= 28.7639 g.

and

Total water present = 14.76×33.7446

$f_2 = \frac{28.7639/10.016}{28.7639/98.082}$

= 4.9807 g.

and

The combined dilution effect will be the active water weighed out = 4.8821 - 0.0012

product of these factors, i.e.

= 4.8809 g.

$F = f_1 f_2 = 0.47553$

(a) effect of water dilution

The specific activity, which is directly

Total water present = 4.9807 g.

proportional to the c.p.m. for a standard filling, will

thus have to be corrected for dilution

Active water present (of original stock solution composition) = 4.8809 g.

Hence the specific activity will be reduced by

a factor $f_1 = 4.8809/4.9807$

The dead time of a counter will depend upon the

(b) effect of exchange with acid.

composition of the filling gas. This is varied

considerably. Total water present = 4.9807 g. assembly

was electronically set at 300 micro seconds which is longer

Total acid present = 28.7639 g.

Hence the specific activity will be reduced by a factor, f_2 , where

$$f_2 = \frac{4.9807/18.016}{4.9807/18.016 + 28.7639/98.082}$$

observed counting rate (x_1) by the relation (94)

The combined dilution effect will be the product of these factors, i.e.

$$F = f_1 f_2 = 0.47553$$

The specific activity, which is directly proportional to the c.p.m. for a standard filling, will thus have to be corrected for these isotopic dilution processes by multiplication with the reciprocal of F

$$\text{or } \frac{1}{F} = 2.1029$$

The dead time of a counter will depend upon the composition of the filling gas (93). As this is varied considerably, the paralysis time of the Geiger assembly was electronically set at 300 micro seconds which is longer

than any likely dead time of the counter. Wherever possible, the counting rate was restricted to low values (2,000 c.p.m.) when the correction for dead time losses would be small.

The true counting rate (x_0) is related to the observed counting rate (x_1) by the relation (94)

$$x_0 = x_1 / (1 - x_1 \tau)$$

where τ is the paralysis time. This relation, with background corrections, was used for every count determined. The alcohol pressure fillings were corrected to 20°C by the application of the gas laws.

The figures obtained for the calibration of the three tritiated stock solutions are given below.

Stock Solution S_I

Sample	Water Alcohol (Weight ratio)	c.p.m. (corrected for background and τ) for standard 3 cm. alcohol filling at 20°C
S ¹ _I	13.9718 x 10 ⁻³	1,013
S ² _I	22.6742 x 10 ⁻³	1,525
S ³ _I	36.974 x 10 ⁻³	2,440
S ⁴ _I	42.1654 x 10 ⁻³	2,799
S ⁵ _I	49.123 x 10 ⁻³	3,335
S ⁶ _I	60.5767 x 10 ⁻³	3,910

These figures were plotted (see fig. 9) and an equation fitted by the method of least squares. The equation obtained was

$$y = 15.6750 \times 10^{-6} x - 1.66407 \times 10^{-3}$$

where y = water/alcohol ratio and x = c.p.m.

Stock Solution S_{II}

Sample	<u>Water</u> Alcohol	c.p.m. (standard filling at 20°C)
S ¹ _{II}	13.8965×10^{-4}	470
S ² _{II}	17.1961×10^{-4}	615
S ³ _{II}	23.1712×10^{-4}	788
S ⁴ _{II}	31.7566×10^{-4}	1,120
S ⁵ _{II}	39.2785×10^{-4}	1,338
S ⁶ _{II}	70.0368×10^{-4}	2,438
S ⁷ _{II}	157.0786×10^{-4}	5,360
S ⁸ _{II}	213.8612×10^{-4}	7,186
S ⁹ _{II}	233.548×10^{-4}	7,935

From fig. 10 then

$$y = 2.95417 \times 10^{-6} x - 35.479 \times 10^{-6}$$

Stock Solution S_{III}

vapour pressure of the solution is calculated by substitution in one of the three equations. The vapour pressure

values were then determined as described in the text.

Sample Water c.p.m. (standard filling at 20°C)
are given below with Alcohol c.p.m. (standard filling at 20°C)

unchanged.

S ¹ _{III}	13.0593 x 10 ⁻⁶	582
S ² _{III}	39.3892 x 10 ⁻⁶	1,829
S ³ _{III}	59.6303 x 10 ⁻⁶	2,653
S ⁴ _{III}	118.6733 x 10 ⁻⁶	5,740
S ⁵ _{III}	203.8824 x 10 ⁻⁶	11,460
S ⁶ _{III}	492.427 x 10 ⁻⁶	26,700

From fig. 11 then

$$y = 1.80988 \times 10^{-8} x + 0.068119 \times 10^{-4}$$

Knowing the c.p.m. for the standard filling and the weight of alcohol introduced to the trap prior to the commencement of a run, the weight of water

vapour frozen out can thus be calculated by substitution in one of the three equations. The vapour pressure values were then determined in an identical manner to that previously indicated (Section III). The results are given below with the symbolic representation unchanged.

Run Number	X_1^*	X_2^*	X_3^*	X_4^*	X_5^*	X_6^*	X_7^*	X_8^*	X_9^*
1	29.375	10.012	3.480	6.897	0.8101	43.72	4.28		
2	29.453	10.012	2.793	3.539	0.8413	43.27	4.30		
3	29.425	10.012	1.890	2.402	1.2710	45.79	4.27		
4	29.272	10.012	2.012	2.537	1.1927	45.82	4.30		
5	29.163	10.012	1.220	1.530	2.0210	45.74	4.29		
6	29.200	10.012	1.780	2.252	1.3541	45.75	4.30		
7	29.141	10.012	2.002	2.544	1.2020	45.99	4.28		
8	29.982	10.012	2.560	3.835	0.9261	45.85	4.28		
9	29.792	10.012	4.500	2.515	1.2114	45.75	4.30		

50.93% Acid from E₁

De = 5.29, m₂+m₃

58.93% Acid from S₁

Run Number	P (")	t (°C)	P ₀ (mm.Hg)	P _m (mm.Hg)	V ₁ (ml.)	Run c.p.m.	Corrected c.p.m.	Weight alcohol (g.)	W calc. (mg.)	P _w (mm.Hg)
1	29.375	18.50	744.04	85.40	10,012	5,420	6,887	0.4301	45.72	4.28 ₀
2	29.453	18.30	746.02	75.89	10,012	2,785	3,539	0.8413	45.27	4.30 ₀
3	29.825	19.10	755.35	86.75	10,012	1,890	2,402	1.2710	45.74	4.27 ₉
4	29.978	20.45	759.05	84.70	10,012	2,012	2,557	1.1927	45.82	4.30 ₂
5	30.165	19.35	764.01	85.90	10,012	1,220	1,550	2.0210	45.74	4.29 ₀
6	30.200	19.75	764.77	84.60	10,012	1,780	2,262	1.3541	45.76	4.30 ₀
7	30.141	18.47	763.45	83.20	10,790	2,002	2,544	1.2820	48.99	4.28 ₀
8	29.982	19.63	759.26	84.70	10,012	2,560	3,253	0.9261	45.68	4.28 ₉
9	29.792	20.21	754.38	83.65	10,012	1,980	2,516	1.2114	45.76	4.30 ₁

Average value of P_w = 4.29₁ mm.Hg.

65.50% Acid From S_I

Run Number	P (#)	t (°C)	P _c (mm.Hg)	P _m (mm.Hg)	V ₁ (ml.)	Run c.p.m.	Corrected c.p.m.	Weight alcohol (g.)	W calo. (mg.)	P _w (mm.Hg)
1	29.236	18.25	740.56	84.50	10,012	900	1,229	1.2619	22.21	2.08 ₈
2	29.579	18.52	749.20	86.00	10,012	1,075	1,468	1.0381	22.16	2.08 ₁
3	29.817	20.23	754.99	80.00	10,012	863	1,178	1.3047	21.92	2.07 ₈
4	30.216	21.53	764.95	83.60	10,012	987	1,348	1.1348	22.09	2.08 ₆
5	30.009	20.68	759.82	82.70	10,012	1,012	1,382	1.1066	22.13	2.09 ₁
6	30.106	19.82	762.38	86.30	10,012	958	1,308	1.1736	22.11	2.07 ₉
7	29.832	18.16	755.52	83.33	10,012	902	1,232	1.2512	22.08	2.08 ₃
8	29.300	17.92	742.19	83.16	10,012	1,050	1,434	1.0618	22.10	2.08 ₂
9	30.291	21.48	766.83	82.61	10,012	980	1,338	1.1445	22.10	2.09 ₀

Average value of P_w = 2.08₄ mm.Hg.

70.00% Acid from S1

Run Number	P (")	t (°C)	P _c (mm.Hg)	P _m (mm.Hg)	V ₁ (ml.)	Run c.p.m.	Corrected c.p.m.	Weight alcohol (g.)	W _{calc.} (mg.)	P _w (mm.Hg)
1	30.046	19.53	760.93	79.80	10,012	458	667	1.2786	11.24	1.068
2	30.673	20.49	776.63	69.19	10,012	454	661	1.2809	11.14	1.077
3	30.358	18.02	768.96	70.10	10,012	412	600	1.4391	11.14	1.075
4	29.981	19.98	759.21	76.00	10,012	388	567	1.5629	11.29	1.079
5	29.810	19.63	754.91	75.90	10,012	520	757	1.1076	11.30	1.080
6	30.102	20.31	762.25	78.00	10,012	505	735	1.1403	11.24	1.071
7	30.302	21.47	767.13	81.20	10,012	498	725	1.1742	11.39	1.081
8	30.016	20.50	760.12	80.31	10,790	472	687	1.3433	12.23	1.078
9	30.106	19.92	762.36	80.60	10,012	430	626	1.3831	11.27	1.070
10	29.984	20.23	759.26	79.80	10,790	418	608	1.5496	12.19	1.075

Average value of P_w = 1.075 mm.Hg.

APPROXIMATE VALUE OF P_w = 1.075 mm.Hg.

75.00% Acid from SII

Run Number	P(")	t (°C)	P (mm.Hg)	P _m (mm.Hg)	V ₁ (ml.)	Run c.p.m.	Corrected c.p.m.	Weight alcohol (g.)	Calc. (mg. x 10)	P _w (mm.Hg)
1	30.302	21.63	767.11	81.24	10,012	590	922	1.6367	44.00	4.180
2	30.146	20.65	763.27	80.60	10,012	470	734	2.0690	44.13	4.195
3	30.218	22.63	764.85	80.70	10,012	512	800	1.8871	43.93	4.176
4	29.796	23.00	754.10	80.00	10,012	750	1,172	1.2782	43.80	4.163
5	29.981	21.86	758.98	79.80	10,012	684	1,069	1.4130	44.12	4.197
6	30.162	20.78	763.68	81.23	10,012	555	867	1.7420	44.00	4.179
7	30.306	23.08	767.03	80.75	10,012	781	1,220	0.9642	44.05	4.188
8	29.978	20.12	759.13	80.10	10,790	491	767	2.1185	47.25	4.169
9	29.861	20.16	756.13	79.90	10,012	592	925	1.6291	43.94	4.178
10	30.179	23.24	763.75	75.18	10,012	676	1,056	1.4169	43.70	4.187

Average value of P_w = 4.181 mm.Hg.

80.14% Acid from S_{II}

Run Number	P(")	t (°C)	P _c (mm.Hg)	P _m (mm.Hg)	V ₁ (ml.)	Run c.p.m.	Corrected c.p.m.	Weight alcohol (g.)	w calc. (mg.)	P _w (mm.Hg)
1	29.919	16.83	757.99	71.20	10,012	317	561	0.7677	1.245	0.120 ₀
2	30.237	17.15	766.04	75.58	10,012	420	743	0.5895	1.273	0.122 ₀
3	30.293	18.71	767.26	73.39	10,012	400	708	0.6172	1.269	0.121 ₉
4	30.116	17.50	762.91	69.74	10,012	369	653	0.6723	1.273	0.123 ₀
5	30.172	18.46	764.24	71.50	10,790	392	693	0.6780	1.364	0.122 ₀
6	29.960	19.72	758.70	72.60	10,012	401	709	0.6163	1.269	0.122 ₀
7	30.212	21.47	764.85	76.10	10,012	387	685	0.6408	1.274	0.122 ₀
8	30.107	20.58	762.31	77.70	10,790	375	663	0.7160	1.377	0.122 ₁
9	30.186	20.98	764.24	77.30	10,012	361	639	0.6894	1.277	0.121 ₉
10	29.824	17.56	755.52	75.10	10,012	407	720	0.6139	1.284	0.123 ₀

Average value of P_w = 0.122₀ mm.Hg.

85.24% Acid From SIII

Run Number	P(")	t (°C)	P _g (mm.Hg)	P _m (mm.Hg)	V ₁ (ml.)	Run c.p.m.	Corrected c.p.m.	Weight alcohol (g.)	calc. (mg. x 10)	10 ² P _w (mm.Hg.)
1	29.425	22.61	744.75	70.34	10,012	17,131	36,025	0.5660	3.729	3.59 ₄
2	29.276	22.47	740.99	70.90	10,012	25,905	54,476	0.3726	3.699	3.56 ₁
3	29.945	19.10	758.29	72.64	10,012	27,420	57,662	0.3537	3.715	3.57 ₃
4	29.876	17.85	756.77	73.10	10,012	11,431	24,038	0.8569	3.728	3.58 ₂
5	30.125	19.18	762.86	72.90	10,790	16,585	34,877	0.6252	3.989	3.56 ₀
6	30.283	20.16	766.85	80.16	10,012	14,163	29,784	0.6881	3.756	3.57 ₆
7	30.172	20.03	764.03	75.12	10,012	13,120	27,590	0.7332	3.711	3.55 ₈
8	30.180	19.82	764.24	73.40	10,790	15,163	31,886	0.6907	4.033	3.59 ₇
9	30.169	17.76	764.21	75.80	10,012	18,108	38,079	0.5339	3.716	3.55 ₉
10	30.085	19.25	702.00	74.16	10,012	12,106	25,458	0.7943	3.714	3.56 ₅

Average value of P_w = 0.0357₃ mm.Hg.

89.82% Acid from S_{III}

Run Number	P (")	t (°C)	P _G (mm.Hg)	P _m (mm.Hg)	V ₁ (ml.)	Run c.p.m.	Corrected c.p.m.	Weight alcohol (g.)	w calc. (mg.x 10)	10 ³ P _w (mm.Hg)
1	30.574	21.30	773.89	69.03	10,012	6,555	17,519	0.1645	5.327	5.157
2	30.523	20.24	772.90	76.80	10,012	15,050	40,222	0.0734	5.395	5.165
3	30.428	20.12	770.48	74.70	10,012	7,750	20,712	0.1414	5.395	5.179
4	30.617	20.65	775.18	74.88	10,012	11,340	30,307	0.0969	5.381	5.171
5	30.312	21.75	767.33	75.60	10,012	8,432	22,535	0.1304	5.408	5.184
6	30.421	21.49	770.13	77.00	10,790	10,580	28,276	0.1126	5.837	5.182
7	30.268	21.76	766.24	76.80	10,012	11,142	29,778	0.0995	5.430	5.195
8	30.174	20.92	763.96	75.80	10,012	8,780	23,465	0.1251	5.397	5.173
9	30.098	20.63	762.08	76.20	10,012	7,812	20,878	0.1404	5.400	5.170
10	30.102	21.32	762.08	75.90	10,790	6,982	18,660	0.1681	5.790	5.145

Average value of P_w = 0.005172 mm.Hg.

94.65% Acid from SIII

Run Number	P(")	t (°C)	P _c (mm.Hg)	P _m (mm.Hg)	V _l (ml.)	Run c.p.m.	Corrected c.p.m.	Weight alcohol (g.)	ω calc. (mg. x 10 ³)	10 ⁴ p _w (mm.Hg)
1	30.807	20.74	780.11	71.00	10,012	1,172	5,417	0.0952	9.982	9.64 ₂
2	30.358	22.47	768.40	64.29	10,012	2,058	9,512	0.0552	9.871	9.61 ₇
3	30.312	19.53	767.66	69.89	10,012	512	2,366	0.2018	10.015	9.67 ₉
4	30.308	23.12	767.06	68.29	10,012	990	4,576	0.1117	10.008	9.69 ₄
5	30.216	21.47	764.95	72.60	10,790	782	3,614	0.1499	10.825	9.66 ₇
6	30.162	20.47	763.70	71.40	10,012	870	4,021	0.1254	9.984	9.62 ₅
7	29.981	21.68	759.18	73.80	10,790	690	3,189	0.1673	10.794	9.61 ₇
8	29.765	19.82	753.57	72.16	10,012	991	4,580	0.1115	9.998	9.61 ₈
9	29.842	18.64	755.85	69.65	10,012	780	3,605	0.1384	9.973	9.63 ₁
10	30.106	21.63	762.23	75.80	10,012	640	2,958	0.1671	10.082	9.65 ₆

Average value of p_w = 0.000965 mm.Hg.

Table 1
 Table 1 shows the vapour pressures and calculated activity over the range 45.68-94.65%

acid obtained by direct measurement. The fourth column gives the water activity calculated (Shankman and Gordon) of Shankman and Gordon (21). The method used in calculating the activities was of interest.

% Acid	p_w (mm.Hg.)	a_w	a_w (Shankman and Gordon)
45.68	10.56 ₇	0.4444	0.4426
51.16	7.75 ₉	0.3263	0.3261
56.08	5.47 ₃	0.2302	0.2300
60.97	3.50 ₇	0.1475	0.1475
<hr/>			
58.93	4.29 ₁	0.1805	0.1798
65.50	2.08 ₄	0.0876 ₄	0.0874 ₀
70.00	1.07 ₅	0.0452 ₂	0.0450 ₂
75.00	0.418 ₁	0.0175 ₉	
80.14	0.122 ₀	0.00513	
85.24	0.0357 ₃	0.00150	
89.82	0.00517	0.000218	
94.65	0.000965	0.0000406	

The results obtained by the tracer technique are again consistently higher, but only differing by 0.3% in activity. It is difficult to account for this discrepancy as the invariable method used by

Table 1 gives the vapour pressures and calculated activity over the range 45.68-94.65% acid obtained by direct measurement. The fourth column gives the water activity calculated from those of Shankman and Gordon (21). The method used in calculating these activities was that of interpolation by mean second differences.

On comparing the results of the proving runs, i.e. the non-radioactive runs in the range 45-60% acid, the water activities are found to differ only in the fourth decimal place; the only exception being the result for the 45.68% acid which differs by 0.3%. The interesting feature arising from these results is the fact that they are consistently higher than those of Shankman and Gordon (21). Their experimental error has been assessed at 0.25% (45) and thus our observed values agree quite closely.

The results obtained from the radioactive tracer technique are again consistently higher, but only differing by 0.3% in activity. It is difficult to account for this discrepancy as the isopiestic method used by

Shankman and Gordon (21) in their measurements is more likely to yield results which are high, due to incomplete removal of gases dissolved in the acid solution.

Incomplete saturation of the nitrogen vapour in our work would not account for this difference either, as the results would then be expected to be consistently low. The possibility of acid or water vapour being carried over in the form of spray is the most likely source of error, in our measurements, especially in the more concentrated acid region where the vapour pressure calculated becomes more sensitive to the amount of moisture trapped out.

Great care was taken to eliminate this possibility by the introduction of spray-traps to the saturator and drastic reductions in the flow-rate of nitrogen gas. Unfortunately, the only means available for checking this process is the results obtained. These were found to be internally consistent within the experimental error of the method.

This error is assessed by considering the individual errors occurring in the method of determining vapour pressures. The volume of nitrogen passing through the line is measured by calibration of the aspirator. Successive calibration figures produced figures that were within 10 ml. volume, the total volume of the aspirator being approximately 10 litres, thus the error would be assessed at $\pm 0.1\%$. The thermostat was maintained at a temperature of $25^{\circ}\text{C} \pm 0.01^{\circ}\text{C}$, fluctuations of this order ($\pm 0.01^{\circ}\text{C}$) would result in an error of $\pm 0.1\%$ depending on the concentration of the acid.

Although the balance used for weighing the absorption trap was sensitive to ± 0.05 mg., weights were not recorded to better ± 0.1 mg. The moisture trapped out ranged from 0.07-0.12 g., thus introducing an error of not more than $\pm 0.14\%$. Errors in reading the manometer attached to the saturator may be similarly calculated to $\pm 0.15\%$.

The individual errors affect the overhaul error

in the vapour pressure determination to different degrees, the latter being most sensitive to accuracy in weighing. The overhaul error in this range (45-60% acid) may be estimated to be $\pm 0.35\%$.

Above 60% acid our results may be compared with those obtained very recently by Glueckauf and Kitt (45). They measured the water vapour pressure up to 86% acid and extrapolated these values up to 88% acid. A glance at Fig. 13 shows that a smoothed curve drawn through our experimental points also passes through their points. Our value for the 85.24% acid being the only one that is removed from this curve.

The values obtained by Deno and Taft (42) in their activity function measurements are also included in this plot (Fig. 13). They do not fit the smoothed curve as closely as those of Glueckauf and Kitt but as their results are not given to an accuracy of better than $\pm 3\%$, then the general agreement is good.

standard deviation (Δ) of the total number of counts is

given by

$$\Delta = \sqrt{N} \quad \dots \dots \dots (7)$$

The accuracy of the vapour pressure measurements employing the tracer techniques is essentially dependent on the method of assay of the tritiated water. Ultimate accuracy in radio-assays is limited by statistical fluctuations inherent in the counting data. It is usual when dealing with experimental data to state the results in terms of the standard deviation. The standard deviation of a single observation is the square root of the average value of the square of the individual deviations. If, for instance, a series of counts ($A_1 \dots A_n$) for n equal intervals of time are made, then it may be shown (95) that the standard deviation (Δ') for the n counts is given by

$$\Delta' = \left[\sum_n (A_n - \bar{A})^2 / n(n-1) \right]^{1/2} \dots \dots \dots (6)$$

where A_n is the individual count, \bar{A} is the arithmetic mean of all the A_n 's and n is the number of times counts are made. If Poisson's distribution law is assumed, the standard deviation (Δ) of the total number of counts is given by

$$\begin{aligned} \Delta &= \left(\sum_n A_n \right)^{1/2} \\ &= \sqrt{N} \dots \dots \dots (7) \end{aligned}$$

where N is the total number of counts made.

These relations are useful in checking experimental data to ensure that the data are truly statistical; when this is the case the statistical errors given by both equations should agree. An example making this clear is given below.

Run	A_n (5 minute periods)	$A_n - \bar{A}$	$(A_n - \bar{A})^2$
1	2589	-0.4	0.16
2	2602	+12.6	158.76
3	2598	+8.6	73.96
4	2500	-89.4	7,992.36
5	2536	-53.4	2,851.56
6	2568	-21.4	457.96
7	2657	+67.6	4,569.0
8	2601	+11.6	134.56
9	2600	+10.6	112.36
10	2643	+53.6	2,872.96

From above table we have

Total counts (N) = 25,894 which is as likely

$$\text{Counting rate (using (7))} = \frac{25,894 \pm \sqrt{25,894}}{50}$$

$$= 518 \pm 3.2 \text{ c.p.m.}$$

deviation Δ as follows (95).

$$\text{Also } \sum_n (A_n - \bar{A})^2 = 19,222$$

$$\begin{aligned} \text{Counting rate [using (6)]} &= 518 \pm \sqrt{5 \left(\frac{19,222}{10 \times 9} \right)^{\frac{1}{2}}} \\ &= 518 \pm 2.9 \text{ c.p.m.} \end{aligned}$$

which is reasonable agreement.

The fact that the results calculated in the two different ways are in reasonable agreement is a good proof that the events were random. If the equipment had manufactured counts (i.e. if there were spurious counts) it would be noted that the positive and negative values of the $(A_n - \bar{A})$'s would not occur with about equal frequency and the standard deviations calculated in the two ways would also not agree.

Two other error units which are in common use are the "probable error" and the "reliable error". The probable error is that error which is as likely to be exceeded as not. The reliable error is that error for which there is a 90% chance of it not being exceeded. These errors are related to N and the mean deviation Δ as follows (95).

Probable error = $0.6745 \Delta = 0.6745 \sqrt{N}$

and the reliable error = $1.64 \Delta = 1.64 \sqrt{N}$

Thus for the above figures the number of counts = $\sim 25,000$

$$\Delta = \sqrt{N} = 0.6\%$$

Probable error = 0.4%

and reliable error = 0.98%.

The total number of counts recorded for any sample was never allowed to fall beneath 25,000 and hence this reliable error of 1% would be applicable to the vapour pressure determinations. Beyond 60% acid, even though individual vapour pressure values tend to differ by less than 1%, it is felt that an accuracy of only this figure (1%) can be justifiably claimed.

The measurement of the water vapour pressure over sulphuric acid solution at 25°C has been completed in the range 45-95% acid. The results of Shankman and Gordon (21) (45-68%) and those of Glueckauf and Kitt (45),

References

- obtained by direct measurements of vapour pressures have been confirmed. The application of a radioactive tracer technique to the air saturation method of (1923), determining vapour pressures has been successfully completed. The results obtained were found to be internally consistent. Comparison of the calculated activities with those of Deno and Taft (42) in the more concentrated acid region (above 70%) showed only moderate agreement. A new method of tritium assay, yielding consistent results, has been proposed and substantiated.
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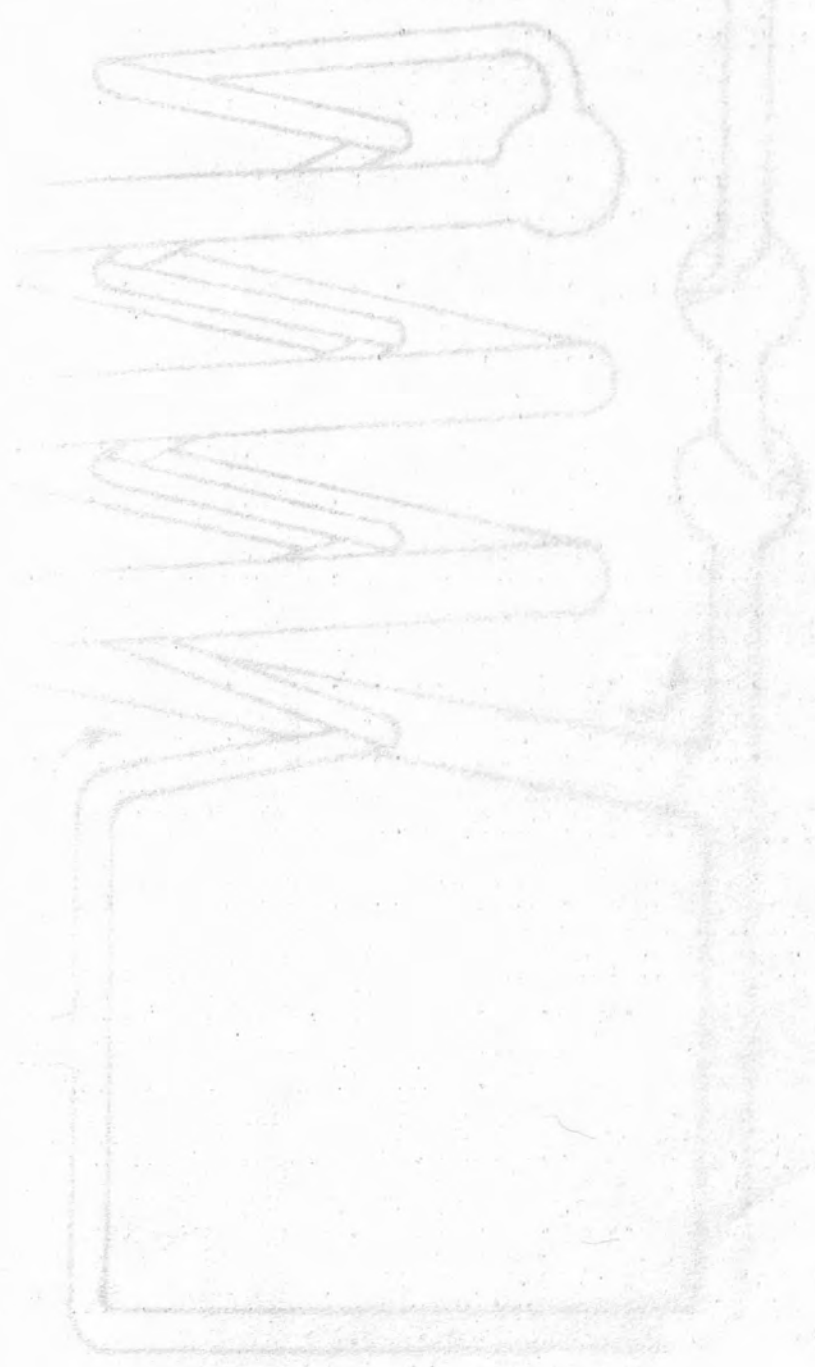
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PRESSURATOR

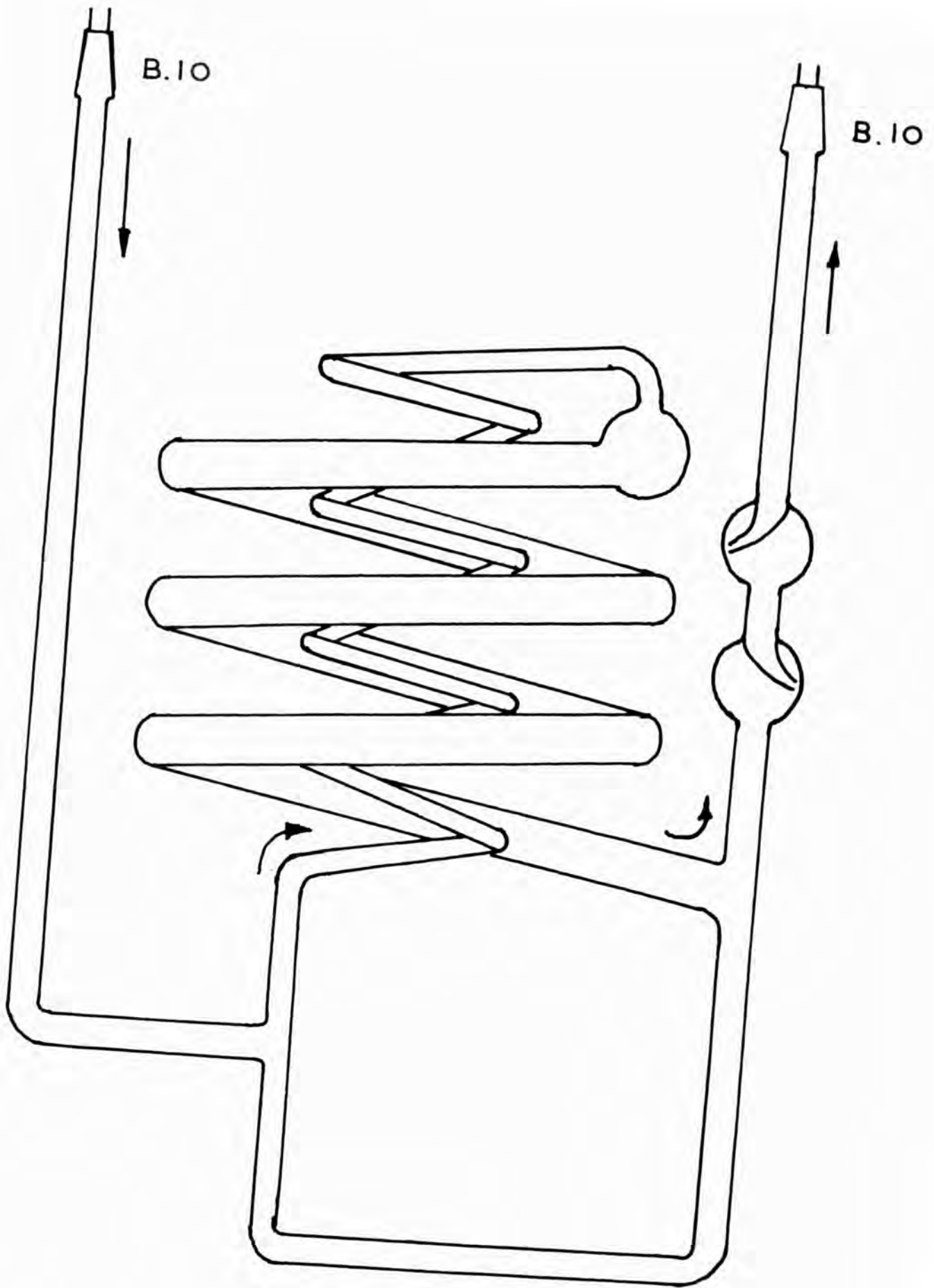


Fig. 1.

PRESATURATOR

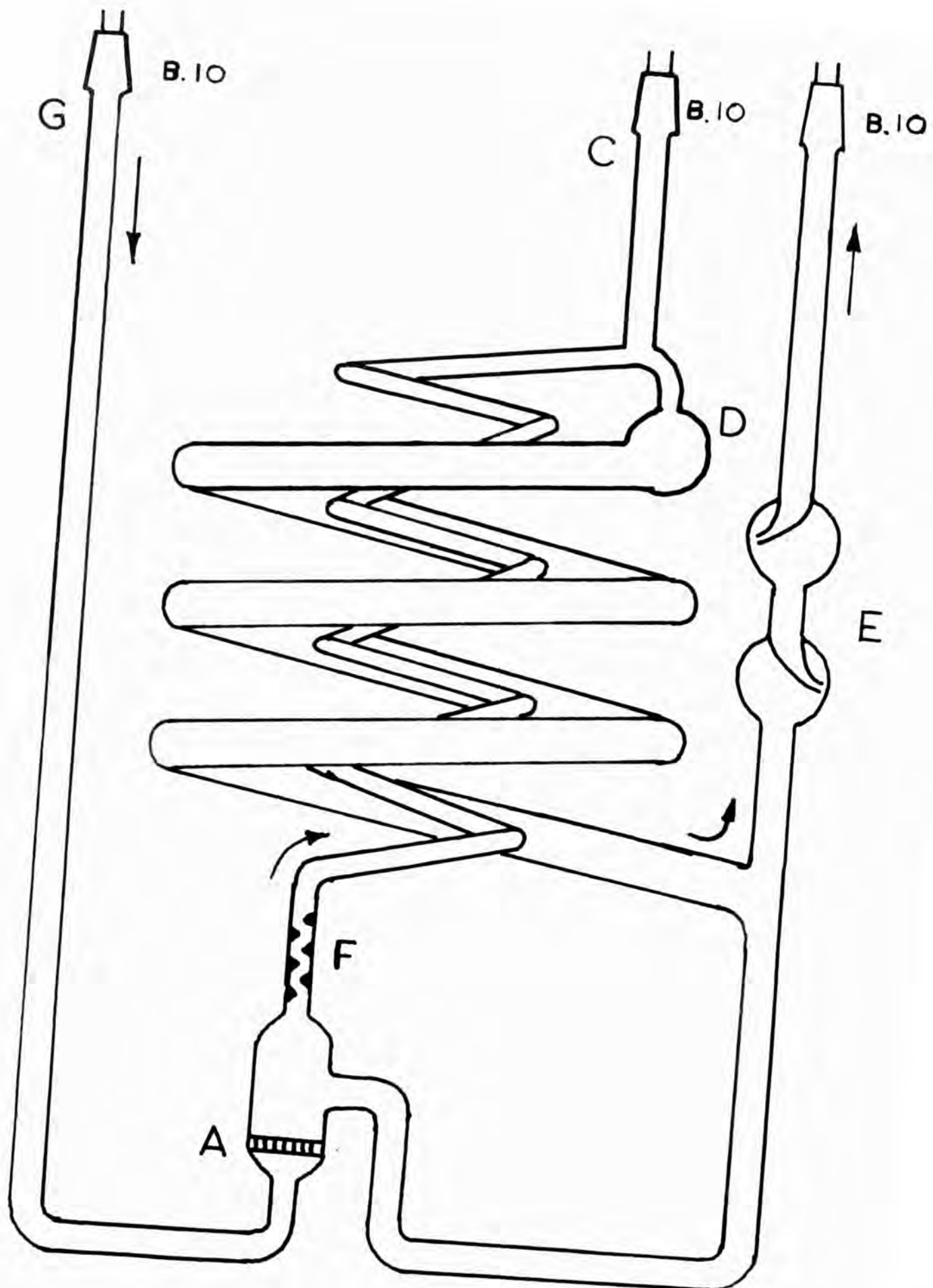


Fig. 2.

SATURATOR

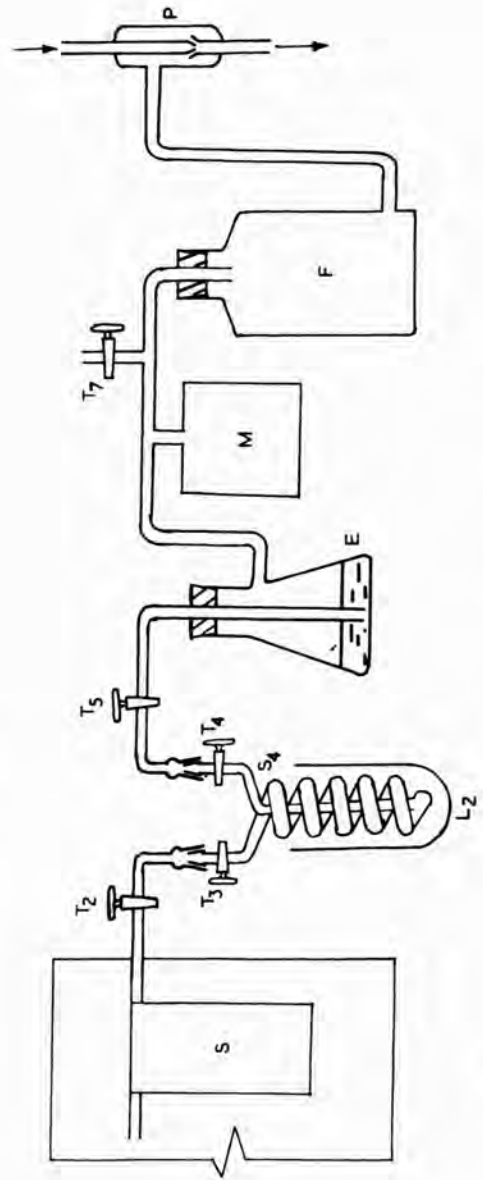
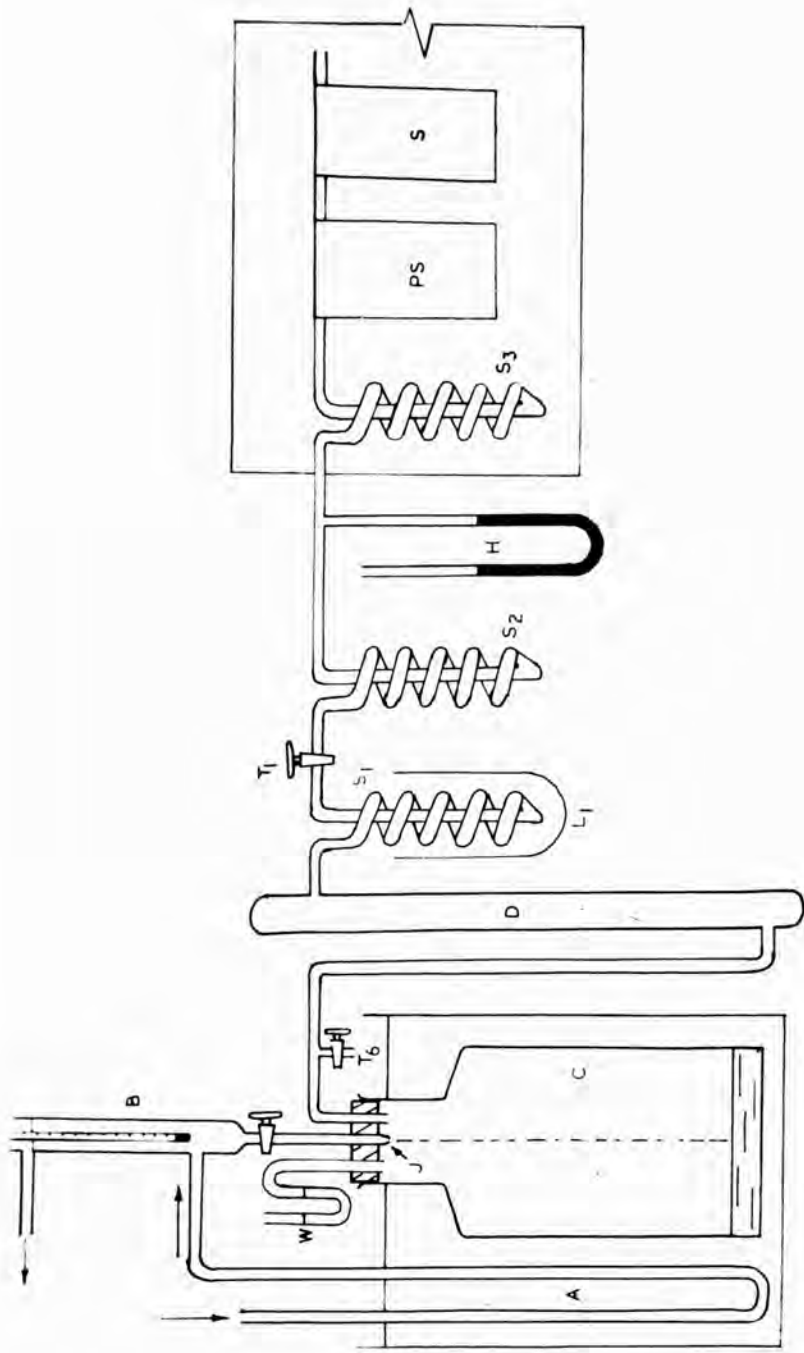


Fig. 3.

VAPOUR PRESSURE LINE

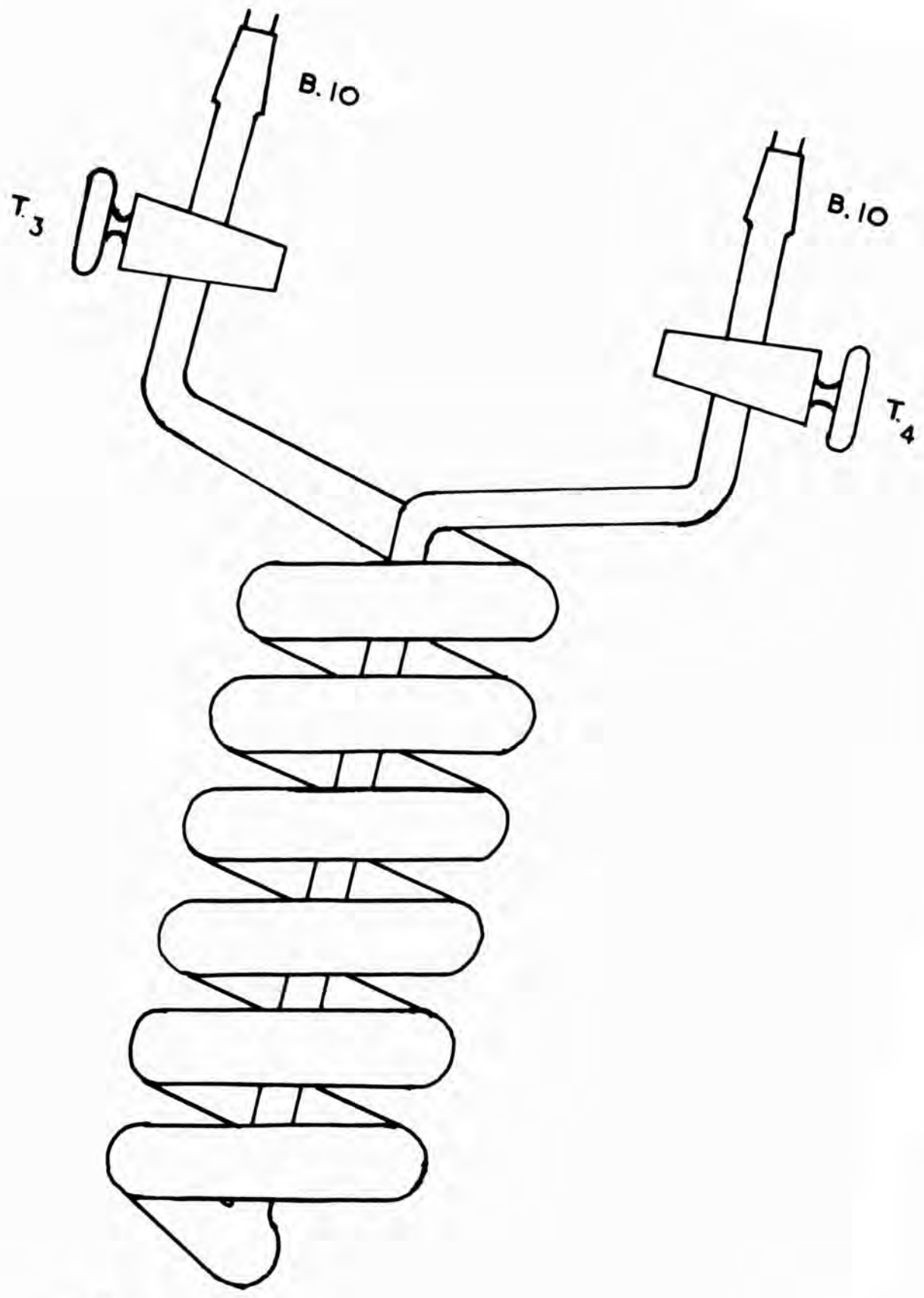


Fig. 4.

WEIGHING TRAP

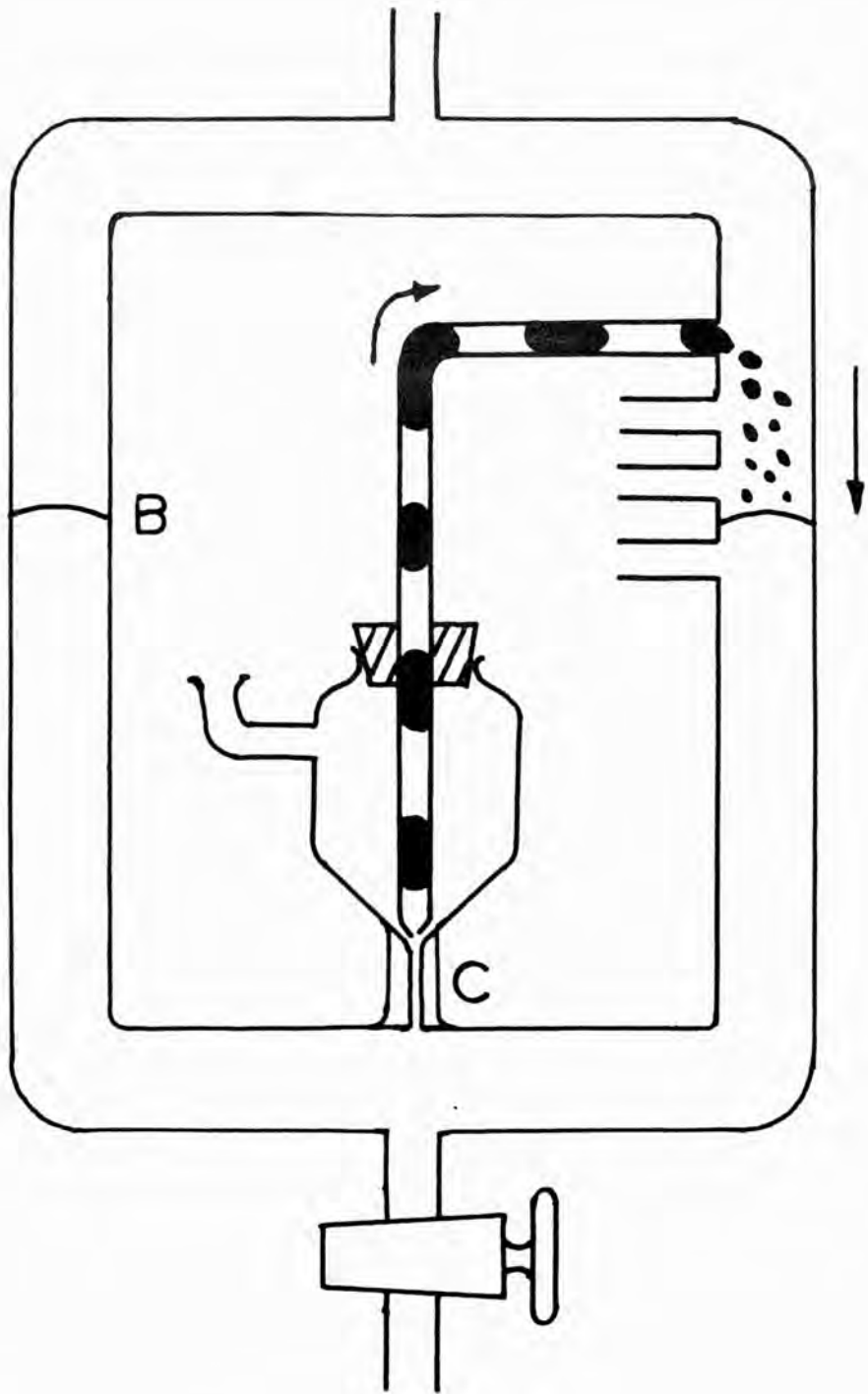


Fig. 5.

MANOSTAT

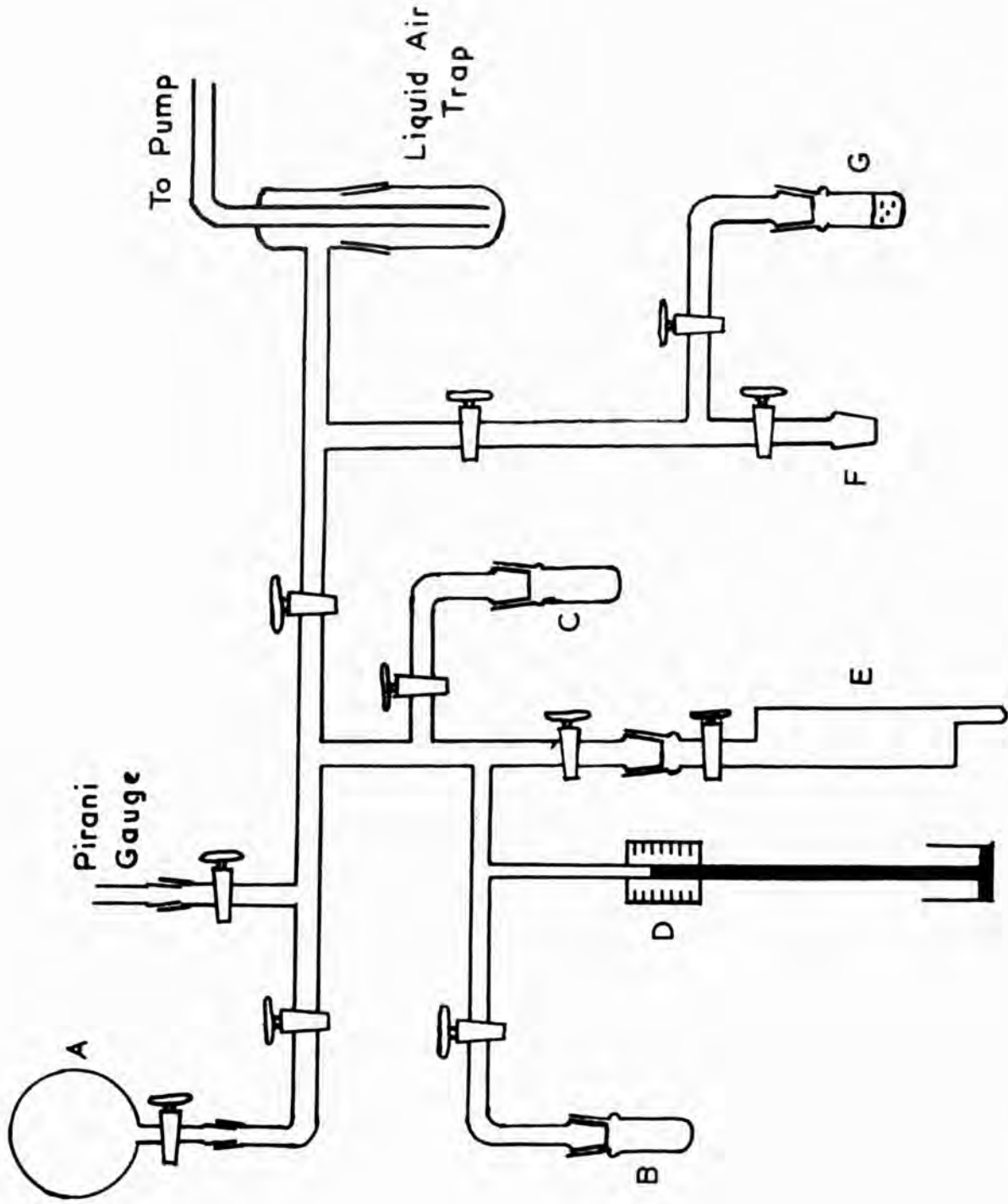
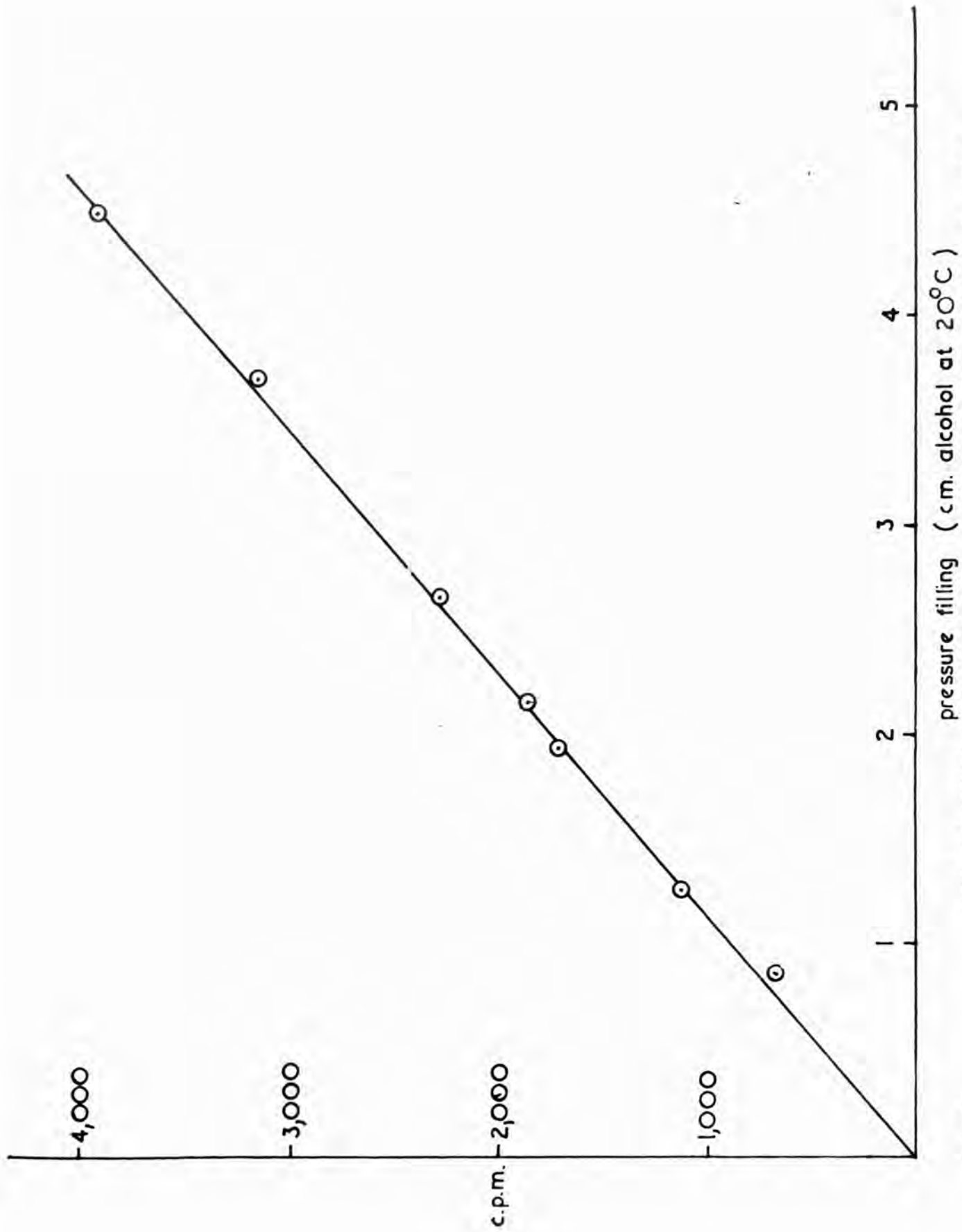


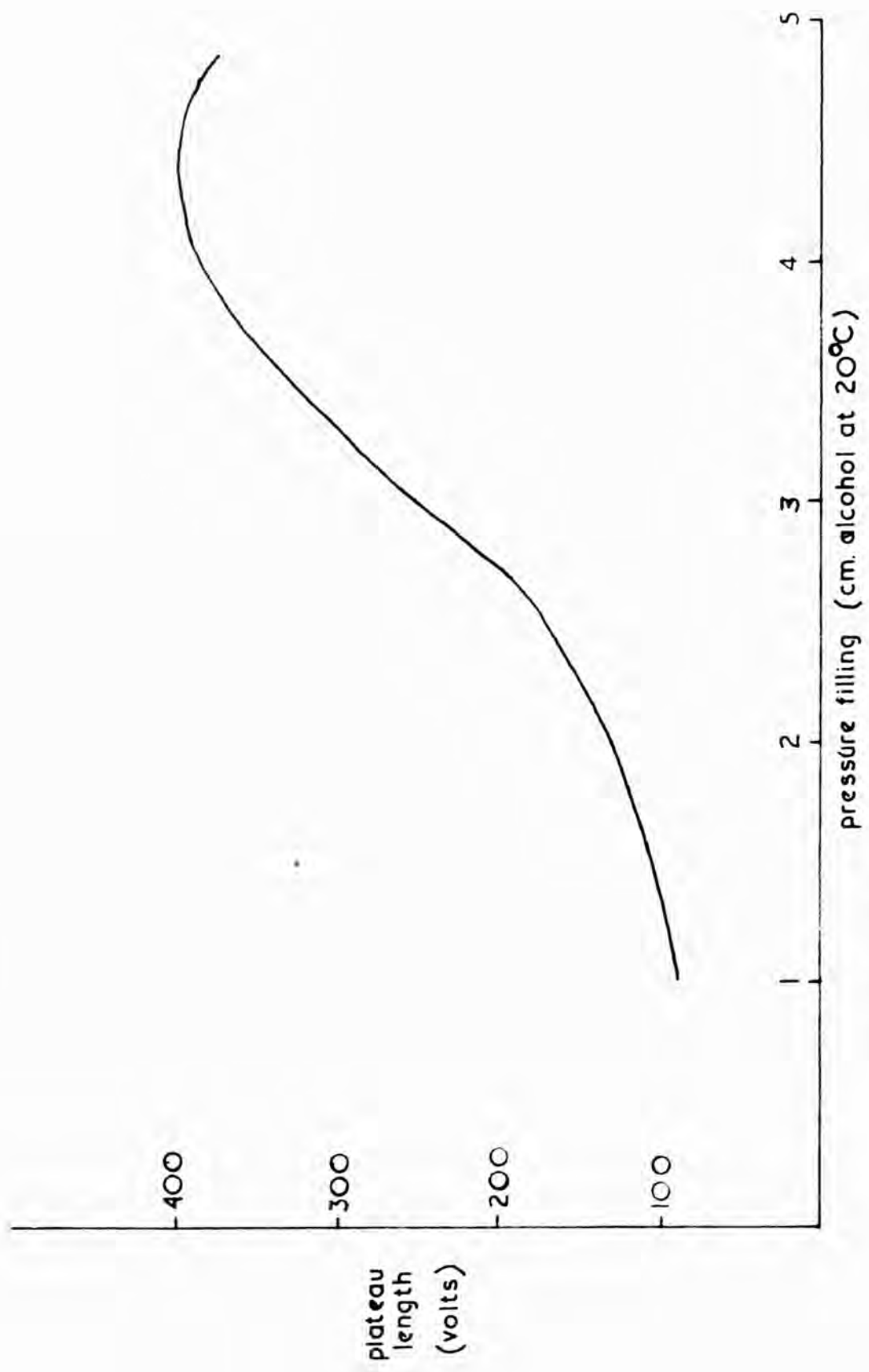
Fig. 6.

VACUUM LINE



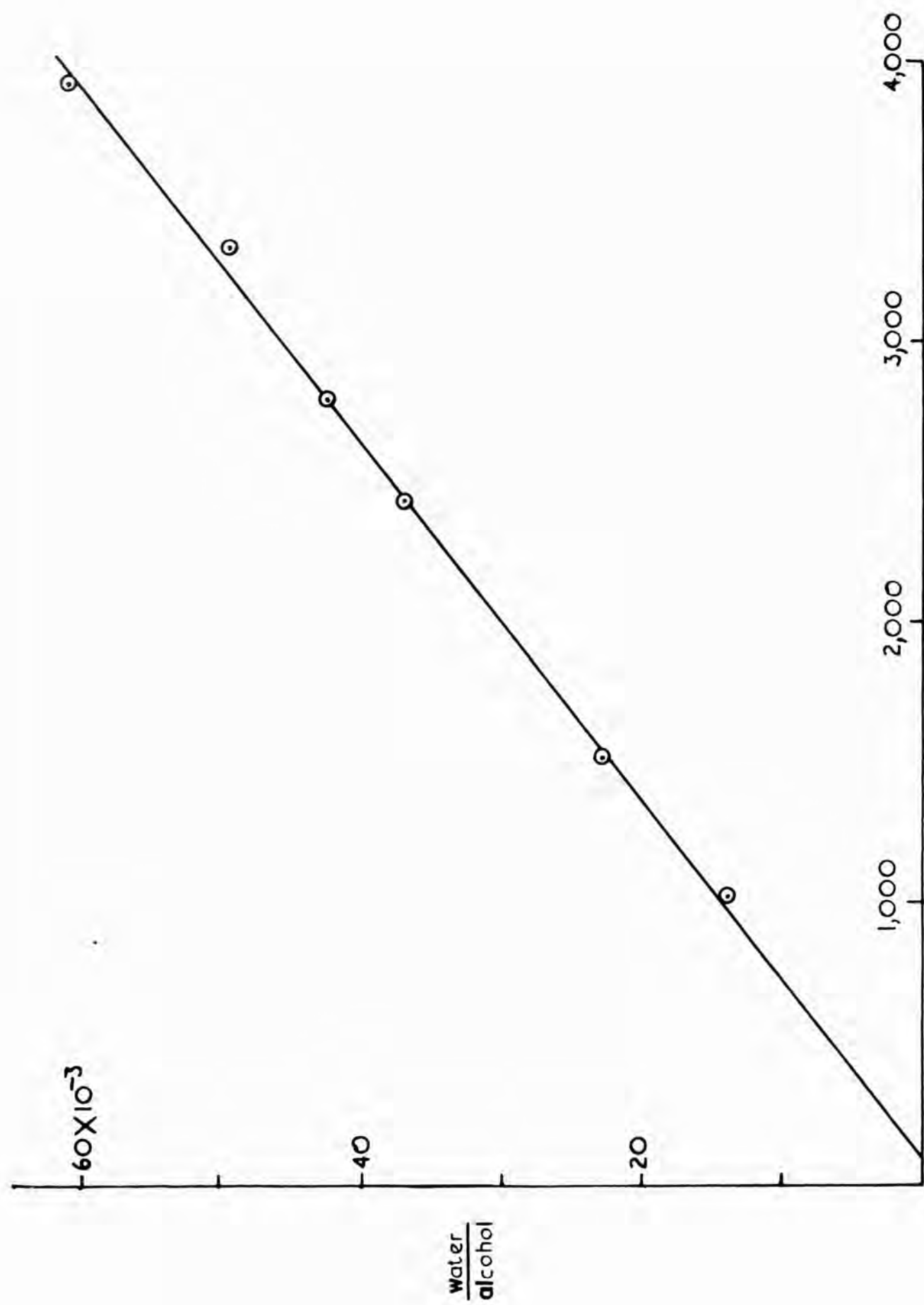
RELATIONSHIP BETWEEN c.p.m. AND PRESSURE FILLING

Fig. 7.



RELATIONSHIP BETWEEN PLATEAU LENGTH AND
PRESSURE FILLING

Fig. 8.



c.p.m. for standard filling (3 cm. alcohol)
 CALIBRATION PLOT OF STOCK SOLUTION S₁

Fig. 9.

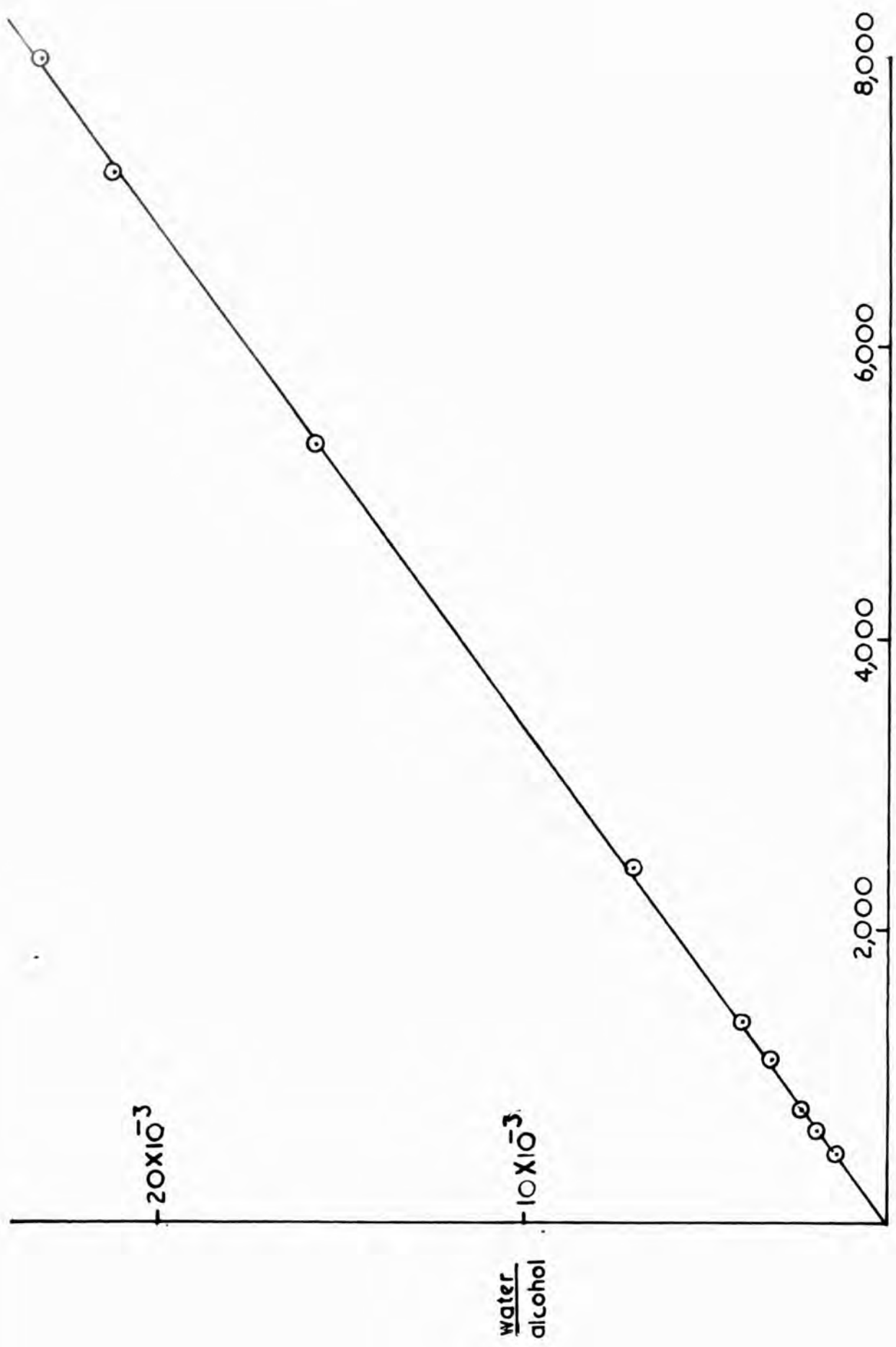


Fig. 10. CALIBRATION PLOT OF STOCK SOLUTION 5 II-

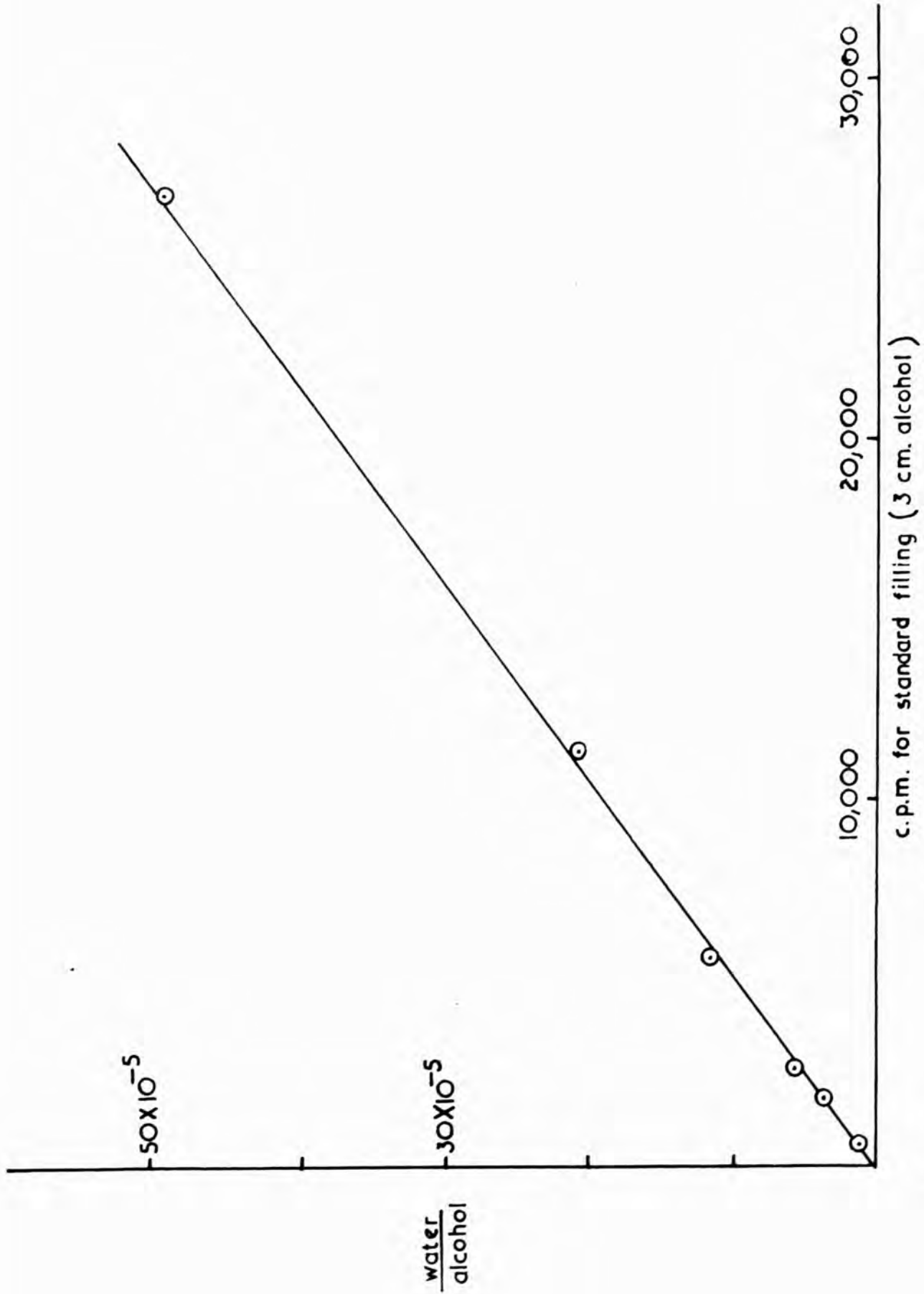
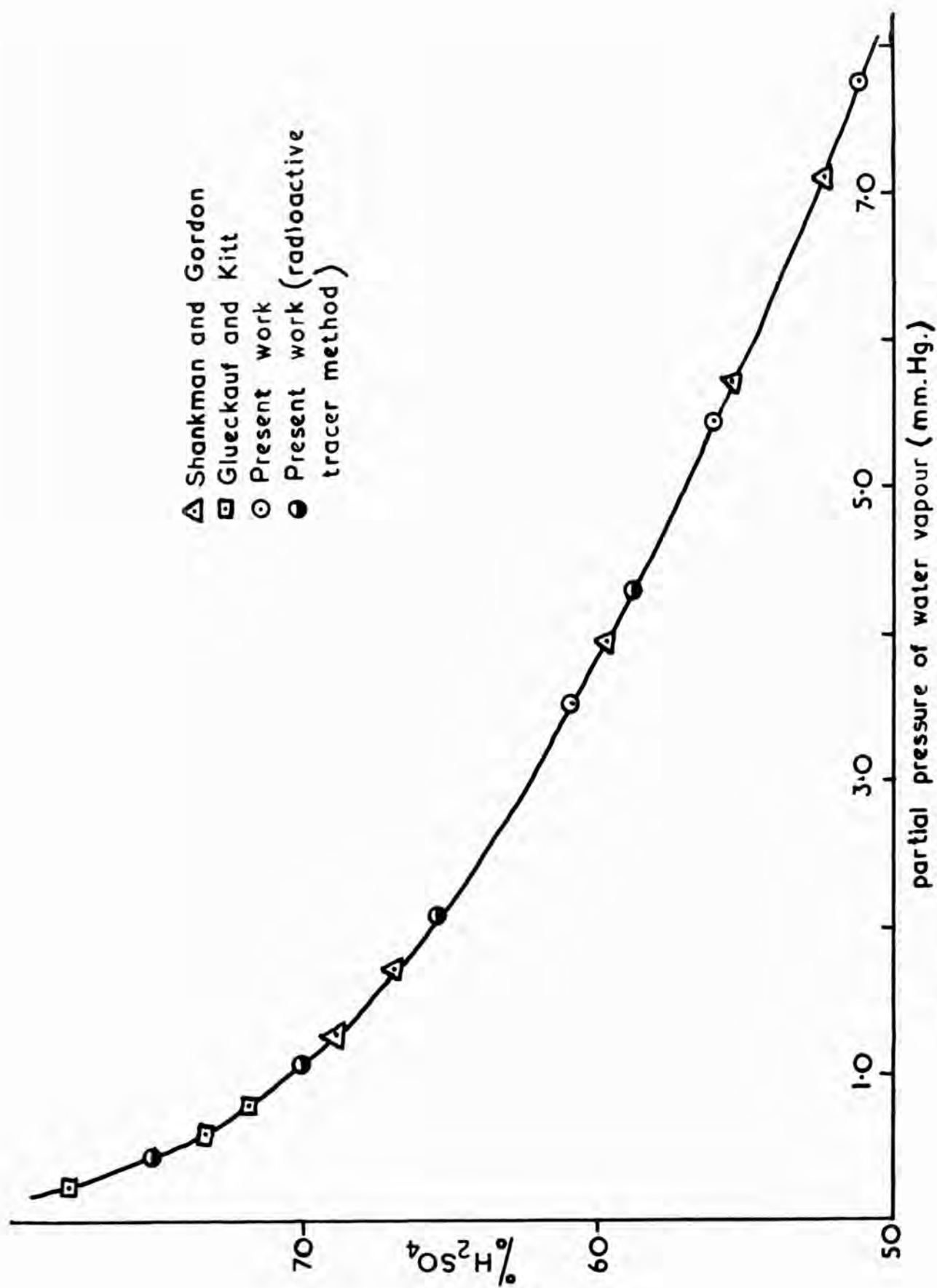
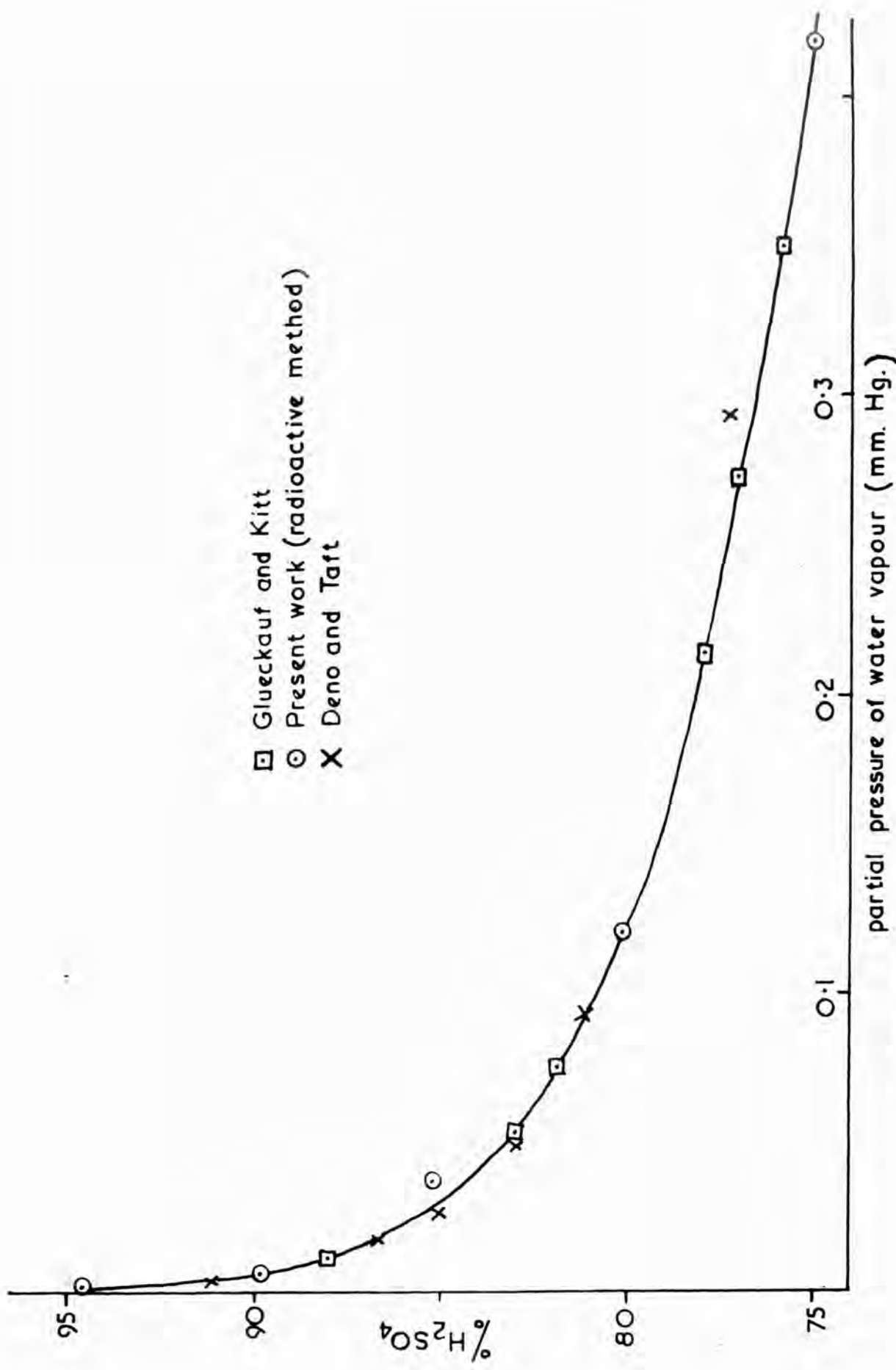


Fig. 11. CALIBRATION PLOT OF STOCK SOLUTION S III—



RELATIONSHIP BETWEEN WATER VAPOUR PRESSURE AND ACID CONCENTRATION 50-75% ACID

Fig. 12.



RELATIONSHIP BETWEEN WATER VAPOUR PRESSURE
AND ACID CONCENTRATION 75-95% —

Fig. 13.