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THE DESIGN AND CONSTRUCTION OF AN APPARATUS
SUITABLE FOR THE MEASUREMENT OF THE
PRESSURE - VOLUME - TEMPERATURE RELATIONS OF GASES

by

JOHN LEONARD GATTENMEYER

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To Whom It May Concern:

This is to certify that the thesis entitled "The Design and Construction of an Apparatus Suitable for the Measurement of the Pressure-Volume-Temperature Relations of Gases" by Mr. John Leonard Gattenmeyer measures up to the required standards of the Master's thesis in this Department.

Yours truly,

-ew

ABSTRACT

An apparatus designed after the fashion of Young and of Kay has been constructed and assembled for the determination of the pressure - volume - temperature relationships of pure compounds up to 200 atmosphere and 360° C.

Pressure measurement depends on the known characteristics of pure nitrogen, and auxiliary apparatus has been assembled for the production and use of this.

Constant temperatures are obtained by boiling under a constant pressure the following compounds: carbon disulfide, chlorobenzene, bromobenzene, aniline, methyl salicylate, 1-bromonaphthalene, and mercury.

These compounds have all been purified and have been used to calibrate a thermocouple for use in the apparatus.

Normal-butanol has been carefully purified for insertion into the apparatus and determination of its pressure - volume - temperature relations and its vapor-pressure.

The theoretical utilization of such data has been discussed.

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THE DESIGN AND CONSTRUCTION OF AN APPARATUS
SUITABLE FOR THE MEASUREMENT OF THE
PRESSURE - VOLUME - TEMPERATURE RELATIONS OF GASES

A. INTRODUCTION

The volume occupied by a real gas under a given temperature and pressure has been the subject of investigation since the middle of the nineteenth century. The careful studies of Regnault and of Amagat showed that real gases do not obey the classical equation $PV = nRT$, the combination of Boyle's and Charles' laws which suitably explains the behaviour of the hypothetical perfect gas.

Since the time of Regnault, two general types of apparatus have been developed for the measurement of volumes at high pressures. One type, using a steel bomb to contain the gas, is suitable for measuring pressure changes of temperature at constant volume. The other type, and the one chosen for this research because of its ease and flexibility of operation, contains the gas sample in a thick-walled capillary where isothermal pressure - volume changes can be visually observed.

Work done in this field up to the present time has been largely concentrated on the petroleum hydrocarbons. This has been almost necessitated because of the tremendous growth

of that industry and the corresponding demand for thermodynamic data on petroleum products for equipment design purposes. The work of Sage and Lacey in this field has been particularly outstanding.

On the other hand, data on the oxygenated hydrocarbons are meagre, and as these compounds are becoming greater in importance because of new synthetic processes, the determination of their thermodynamic properties is desirable.

As a consequence, the first step towards initiating a program of research along this line, is to assemble an apparatus suitable for such determinations.

This thesis describes in detail the design and construction of apparatus for the determination of pressure - volume - temperature relationships up to 200 atmospheres and 360° C. and of vapor-pressures over the same range.

In keeping with the programme of the study of the oxygen containing organic compounds, some progress has already been made in preparing the apparatus for P-V-T determinations on normal-butyl alcohol.

B. THEORETICAL DISCUSSION

(1) The Pressure - Volume - Temperature Relations of a Real Gas.

Ever since the studies of Regnault proved that real gases do not obey the simple gas law, efforts have been made to develop an universal equation to describe state behaviour. The best that can be done is to represent the P-V-T data of a single compound with an equation the constants of which must be arbitrarily determined. Further, the better the data are represented by different equations the more mathematically cumbersome and arbitrary do they become.

One of the first theoretically derived equations of state was that of Van der Waals. Its derivation is based on two general concepts not applicable to the perfect gas. The first of these is the fact that gas molecules occupy finite volume whereas no such condition is stipulated for the perfect gas. The volume available for free movement accordingly is not V the total volume, but $V-b$, where b is representative of the volume of the molecules.

The second concept recognizes the forces of attraction and repulsion between molecules which is not applicable to the molecules of a perfect gas. Because the molecules on the boundaries of a vessel are attracted inwards by a force proportional to the square of the number of molecules present per unit volume, the real pressure in a gas exceeds the measured pressure P by a term a/V^2 which is proportional to the square of the density.

The new volume and pressure factors when substituted in the perfect gas equation give,

$$(p + a/V^2) (V - b) = RT$$

The Van der Waals equation has been found more accurate than the simple gas equation, but nevertheless deviations of large magnitude occur for most gases to which the equation has been fitted.

Two other equations, both similar to the Van der Waals equation in their general form and in the number of constants they contain, are the Dieterici(21).

$$p = \frac{RT}{V - b} e^{-\frac{a}{RTV}}$$

and the Berthelot,

$$p = \frac{RT}{V - b} - \frac{a}{TV^2}$$

Although the Dieterici is somewhat arbitrary, the Berthelot recognizes the variation of intermolecular forces with temperature with the term a/TV^2 .

Although either equation may represent given data better than does the Van der Waals, it cannot be said that they are better than the Van der Waals.

The three equations so far mentioned are of further theoretical interest because they can be put in what is known as the reduced form. Such a reduced equation contains no arbitrary constants, but instead three constants characteristic of a given substance, namely the critical volume, temperature and pressure. The arbitrary constants "a" and "b" may be found in the terms of the critical constants from the following identities,

$$\left(\frac{\partial P}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

which hold at the critical point.

Theoretically a reduced equation will represent the data of any substance, and all that is required to be known about the substance are its critical constants. Although the three reduced equations of state cannot represent data any better than the equations of state themselves, they have been found extremely useful for approximate calculations where no other data are available.

An equation which, according to the calculations of its originator represents data exceedingly well over wide ranges, is the Wohl equation (22),

$$P = \frac{RT}{V-b} - \frac{a}{V(V-b)} + \frac{C}{V^3}$$

It is of further interest because it contains only three constants which can all be expressed in terms of the critical constants.

The Keyes equation (23),

$$P = \frac{RT}{V-B} e^{-\alpha/V} - \frac{A}{(V-1)^2}$$

contains four constants and represents data well over wide ranges.

The Beattie-Bridgeman equation (24),

$$P = \frac{RT(1 - \frac{c}{VT^3})}{v^2} \left(v + B_0 \left(1 - \frac{b}{v}\right) \right) - \frac{A_0 \left(1 - \frac{a}{v}\right)}{v^2}$$

contains five constants and is rather cumbersome. It represents data within experimental accuracy, but has been found

unsatisfactory for extrapolation.

Many more equations have been proposed but as these have not been successful in the representation of data, or as they are arbitrary in their derivation, there is little point in discussing them.

(2) Vapor-Pressure Concepts.

According to the phase rule, when two phases are present in a one component system, there is one degree of freedom. Vapor-pressure is then dependent upon the temperature as is the volume, and stipulation of the volume is not necessary when presenting such data.

The basis of most vapor-pressure equations is the Clapeyron differential equation,

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$

where

ΔH = enthalpy of change of state

ΔV = volume change of state

Integration depends upon expressing ΔH and ΔV in terms of the other two variables and in order to integrate, three assumptions are usually made; (1) that the latent heat remains constant with temperature, (2) that the liquid volume is negligible compared to the vapor volume, and (3) that the perfect gas law is obeyed in the gas phase.

Integration then yields;

$$\ln P = -\frac{\Delta H}{RT} + K$$

If an arbitrary constant is substituted for ΔH it has been found that the equation is satisfactory for many compounds from the triple point to the critical point despite the many approximations in its derivation. For closer representation of experimental data other equations must be resorted to.

If it is assumed that the heat of vaporization is linearly dependent upon temperature the following equation, originally derived by Rankine (26), is obtained,

$$\ln P = - \frac{a}{T} + b \log T + C$$

Its accuracy is better than the first equation as would be expected.

The empirically derived Antoine equation (27) has been found by Thomson (25) to fit vapor-pressure data of many liquids extremely well up to reduced temperatures of 0.85 .

The Antoine equation is,

$$\log P = A - \frac{B}{t + C}$$

Although A, B and C are empirical constants, it has been found that C equals 230 for a large number of organic compounds and that rarely does C equal more than 240 or less than 220. "t" is the temperature on the centigrade scale.

It is seen then, that the pressure - temperature relations of a real gas in equilibrium with its liquid are best expressed by empirical equations based on theoretical considerations, as are the P - V - T relations of a real gas.

(3) The Extension of Thermodynamic Data.

Pressure - volume - temperature data has found a practical use in applied Chemical Engineering. Not only is this data of value in itself for such things as the calculation of the dimensions of a gas storage vessel, but it is the foundation of the thermodynamic network relating the familiar energy quantities enthalpy, entropy and internal energy to pressure and temperature. Once the volume has been defined at given temperatures and pressures, it should be theoretically possible to define all other thermodynamic properties, for the stipulation of only three variables defines any one phase system of constant composition.

Variables in the two phase region may be determined from vapor-pressure data.

The various heat quantities are all related to pressure, temperature, and volume by readily derived thermodynamic identities. Such data when derived are usually tabulated, or plotted graphically. Three types of graphs are commonly used; these are the pressure - enthalpy (P - H) diagram, the temperature - entropy (T - S) diagram, and the enthalpy - entropy (H - S) or Mollier diagram.

The Pressure - Enthalpy Diagram

Qualitatively the enthalpy usually increases with temperature and decreases with pressure.

The basic equation for relating enthalpy changes to other variables is,

$$\Delta H = \int_{T_0}^T C_{pd}T + \int_{P_0}^P \left\{ V - T \left(\frac{\partial V}{\partial T} \right)_P \right\} dP$$

This gives the enthalpy change for a given pressure and temperature change. If the specific heat and P - V - T data are expressed in an equation it may be possible to integrate the equation analytically.

If it is desired to obtain the isothermal change of enthalpy, the equation simplifies to,

$$\Delta H = \int_{P_0}^P \left\{ V - T \left(\frac{\partial V}{\partial T} \right)_P \right\} dP$$

If P - V - T data can be fitted accurately to a volume-explicit equation the above equation may be integrated. An excellent means of carrying out such an integration was used by Kvalnes and Gaddy (28). Robinson and Bliss (29) illustrated how isothermal enthalpy changes may be evaluated with such pressure-explicit equations of state as those of Van der Waals, Wohl, and Beattie and Bridgeman.

With Joule-Thompson measurements and specific heat data, use can be made of the following equation for enthalpy changes (30),

$$\left(\frac{\partial H}{\partial P} \right)_T = - C_p \left(\frac{\partial T}{\partial P} \right)_H$$

Enthalpy changes in the two phase region can be determined from the Clapeyron equation. The best values are obtained by using the unintegrated form and determining $\frac{dP}{dT}$ as accurately as possible either graphically or from a differentiated vapor pressure equation accurately representing the data. Thompson (28) recommends the differentiated Antoine

equation for this purpose. Experimental liquid and vapor-volume data up to the critical point are also required.

The Temperature - Entropy Diagram

The entropy for the saturated liquid can be obtained from the following equation,

$$s = \int_{T_0}^T \frac{dH}{T} - \int_{P_0}^P \frac{V_L}{T} dP$$

where enthalpy values are determined as described in the last section.

The entropy of the saturated vapor is determined by adding to the saturated liquid value, the entropy of vaporization which is calculated by dividing the latent heat by the temperature.

Isotherms may be extended into the superheated region by means of the following identity,

$$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

which is similar to the enthalpy equation already described.

The Mollier Diagram

The Mollier diagram, a plot of enthalpy vs. entropy, may be easily constructed from values determined in the previous sections.

C. APPARATUS

(1) Types in General Use.

There are essentially two types of apparatus for the measurement of pressure - volume - temperature relations at high pressure: one a constant volume device, the other a constant temperature device.

(a) The Constant Volume Apparatus.

Variation of pressure with temperature can be measured by the apparatus developed by Keyes (1). It consists of a steel bomb in which the sample is contained over mercury. Pressure is measured with a dead weight piston gage, and temperature is maintained by a thermostat. Pressure determinations are made at various temperatures.

This type of apparatus was used by Beattie (2) and by Sage (3) and is capable of measuring pressures up to 10,000 p.s.i. (4).

(b) The Constant Temperature Apparatus.

Pressure - volume isotherms may be determined by an apparatus originally used by Andrews (5). It was extensively developed by Young (6) and was used by Kay (7), Sage (8), and others (9, 10).

(2) General Description of the Apparatus.

In brief, the apparatus consists of a compressor, bolted in a horizontal position, with three vertical branches each containing a thick-walled capillary tube sealed at the

top. Contained in one capillary over mercury, is a sample of the substance under investigation. The pressure is applied by means of a threaded piston manually operated, and measured by means of the two other capillaries containing a reference standard for which the pressure - volume data are known at a given temperature. Temperature is maintained constant on the test sample by means of the vapor of a pure organic compound boiling under a constant, reduced pressure.

Equilibrium between liquid and vapor is brought about by a magnetically operated stirrer when making determinations in the two phase region.

The volume occupied by the sample is determined by measuring the height of mercury in the previously calibrated capillary by means of a cathetometer.

The method is thus not only appropriate for the measurement of pressure - volume relations at constant temperature but for the determination of vapor-pressures, orthobaric densities, and critical constants of one or more component systems.

(3) Construction and Operation of the Apparatus.

(a) The Application and Measurement of Pressure.

The apparatus is illustrated in Fig. I.

Steel compressor block A was constructed from a piece of 4 in. by 4 in. bar stock, 18 in. long. Pressure may be applied to the mercury contained in A by screwing threaded piston C into block. Leakage along the piston is avoided by means of gland E, which was packed at L with graphite-

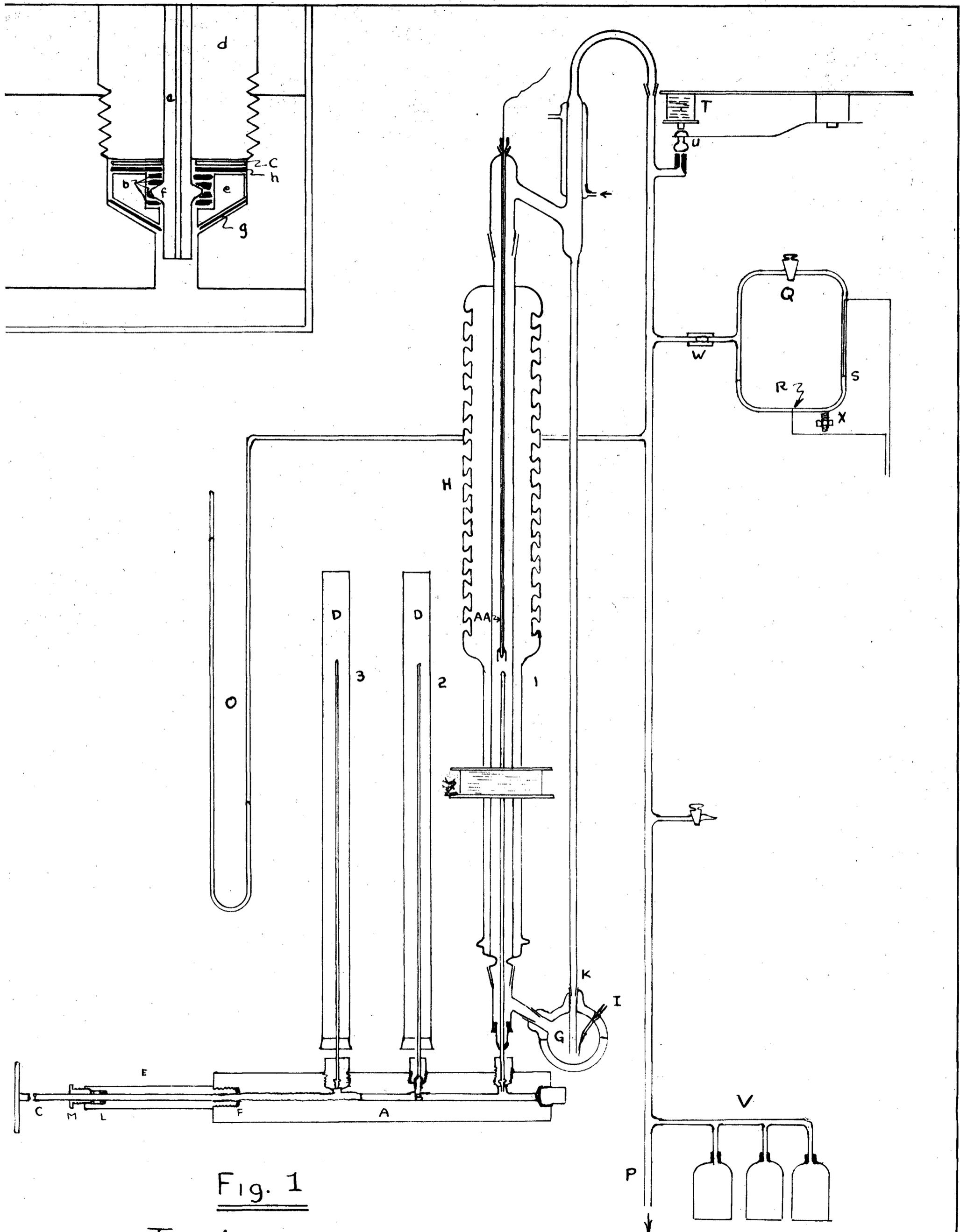


Fig. 1

THE APPARATUS

impregnated twine (Johns-Manville Mogul Coil Packing) held in place by nut M bearing on a loose fitting steel sleeve. Rubber washers backed by an aluminum washer served to keep joint F leak-proof.

Three pressure cells, consisting of three thick-walled, "true-bore" capillaries are designated by 1, 2 and 3.

Each capillary was 2 mm. in inside diameter, 8 mm. in outside diameter, and 35 in. long.

Capillary 1 contained the sample under investigation, while 2 and 3 contained pure nitrogen, the reference standard. Capillary 3 is used for low pressure measurements, while 2, which has an enlargement at the bottom to contain nitrogen at low pressures serves as a high pressure gage.

Capillary 3 was calibrated for pressure measurement by means of a mercury manometer in position 2, and capillary 2 was calibrated for high ^{measurement} pressure ~~at~~ by noticing the mercury level in 3 and 2 simultaneously at some suitable intermediate pressure.

Both nitrogen-containing capillaries are maintained at 0° C. by means of an ice-water bath (D) surrounding them, and deviations of nitrogen from the gas law are corrected for by using the data of Smith and Taylor (11) fitted to the Keyes equation. This data agrees well within the accuracy required, with the data of Bartlett (12), Amagat (13), Holborn (14), Verschoyle (15), Onnes (16) and Michels (17).

The details of the packing for capillaries 1 and 3 are shown in the insert. The capillaries are secured by

nut "d", steel washer "c", and rubber washers "h", bearing against enlargement "f" on the capillary. The enlargement is cushioned in steel cup "e" with rubber washers "b". Leakage around the cup is avoided by means of rubber washer "g".

(b) The Maintenance and Measurement of Temperature.

The temperature is maintained constant around capillary 1 with the vapor of a pure organic compound boiling under a fixed, reduced pressure. The liquids originally used by Young (18) for this purpose are used. The entire range of temperature from 25°C. to 358°C. can be obtained by boiling the following liquids under various pressures up to atmospheric.

Compound	Lower Temperature °C.	Higher Temperature °C.
Carbon disulfide	25	46
Ethyl alcohol	47	78
Chlorobenzene	79	132
Bromobenzene	133	155
Aniline	156	184
Methyl salicylate	185	222
1-bromonaphthalene	223	280
Mercury	281	358

The higher temperature is the approximate normal boiling point of the compound. The lower temperature was obtained by reducing the pressure.

The bath itself consists of a vacuum-jacketted distillation column (H) which is completely silvered except for two vertical observation strips diametrically opposed. The column is four feet long and one inch in internal diameter. Expansion bellows on the upper half of the column are designed to accommodate a temperature differential of 340°C . from the inner to the outer column. The useful length of the column is two feet.

Vapors rise into the column from the 500 ml. boiling flask (G) and condensate returns at (K). Attachment (I) consisting of a finely drawn out tube inserted through a standard taper joint serves to avoid bumping in the boiling liquid.

Heat is supplied to the flask by means of an asbestos insulated, nichrome, heating mantle connected to a variac and capable of delivering 300 watts at 110 volts. The upper half of the flask, and the side arm to the column are heated with a nichrome element insulated with asbestos. The maximum heat input to this element is 200 watts.

In order to maintain the pressure and thus the temperature constant, a manostat after that of McConnell (19) was constructed.

It consists of glass hoop (R), constructed from 10 mm. diameter pyrex tubing, electromagnet activated bleed valve (U) and an electronic relay (Fig. II).

While the apparatus is being evacuated by means of an aspirator, the cock (Q) is closed at the required pressure. As evacuation continues, the sulfuric acid contained in the hoop

rises in the left leg breaking contact at (S). This activates the relay magnet (Fig. II) and causes the electromagnet to pull up the plunger covering the 2 mm. opening. When the air rushes in, contact at (S) is remade and the relay shuts off the valve.

Sudden pressure pulses are dampened by surge bottles (V) and the absolute pressure is indicated by manometer (O).

Several improvements upon the original suggestions of McConnell have been incorporated to give a greater degree of control and to facilitate the setting of the apparatus.

Sulfuric acid of specific gravity 1.71 has been suggested by Morton (20) as being more sensitive than mercury because of its lower density. In addition it is not contaminated on its surface as is mercury.

Although a coarse adjustment can be obtained by closing cock (Q), a finer adjustment was found necessary and was incorporated in the form of a flexible tube (W) and screw adjustment (X) by which the glass hoop could be rotated about the flexible tube as centre. In this way extremely small changes in pressure could be obtained by merely adjusting (X) with (Q) closed.

Bleed valve plunger (U) consists of a brass strap serving as a spring and a lever arm to which is secured a bolt covered with a soft rubber pad.

It was found necessary to use an electronic relay because the tungsten - sulfuric acid contact resistance was extremely high and because electrolysis of the sulfuric acid

OUTPUT TO BLEED VALVE

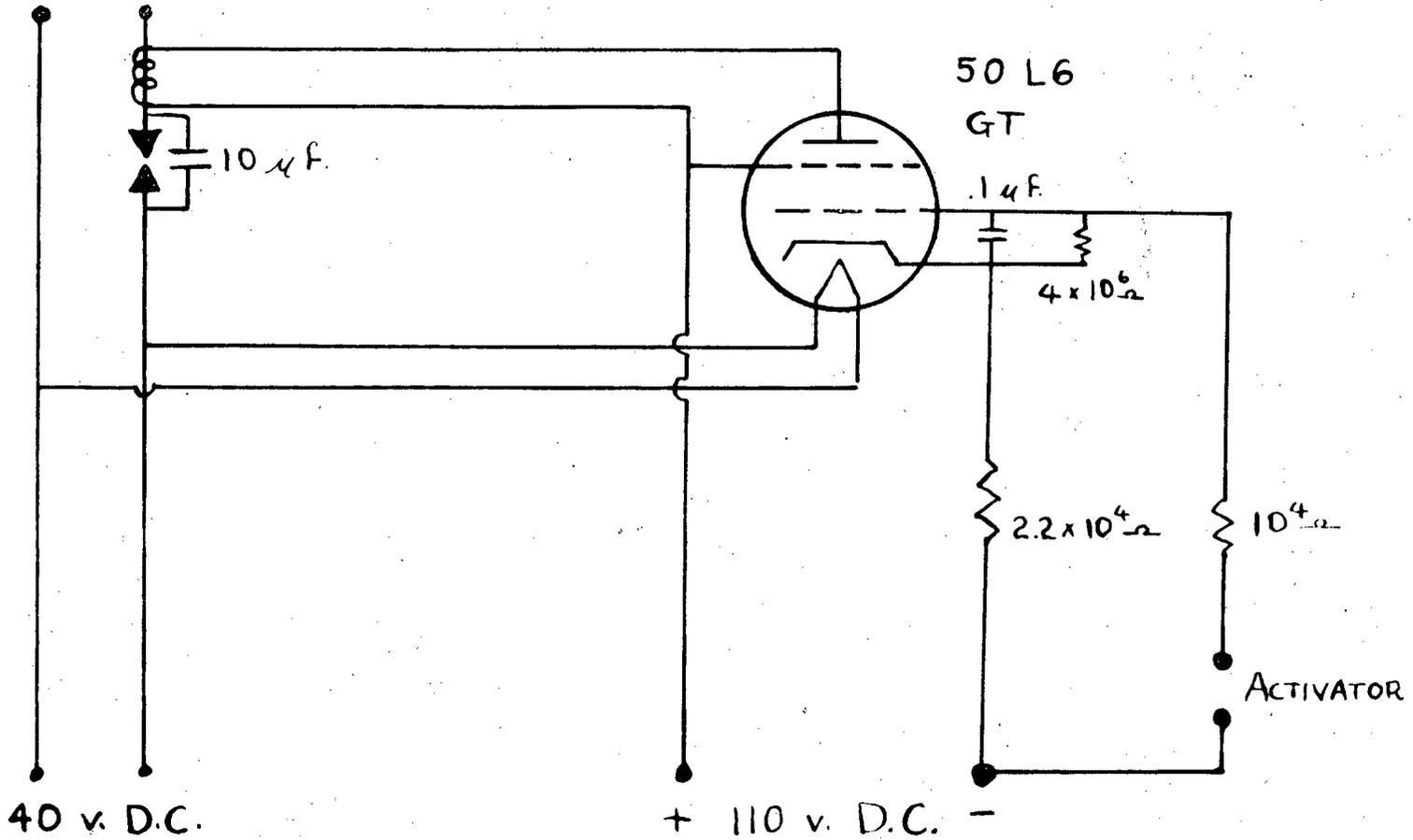


Fig. 2

CIRCUIT DIAGRAM OF THE ELECTRONIC RELAY

would occur at finite current and disturb the setting of the hoop.

A circuit diagram of the relay is shown in Fig. II. Its main features consist of the 50L6 GT pentode, and an electromagnet operated circuit breaker. Forty volt direct current is made and broken as contact is broken and made by the activator changing the grid bias.

The temperature of the vapor bath was measured to the nearest 0.1°C. by means of a copper constantan thermel previously calibrated over the range of use, and a Leeds and Northrup type K-2 potentiometer (see Procedures).

The thermel was constructed from Leeds and Northrup glass insulated thermel wire, and was protected from the vapor by a pyrex tube (AA) the end of which was blown very thin and protected from condensate by a shield.

(c) The Measurement of Volume.

The volume occupied by the samples in the capillary was determined by measuring the level of the mercury with a cathetometer. This height was translated into volume using the calibration data previously obtained.

(d) Construction and Operation of the Stirring Device.

To bring about speedy equilibrium in tube 1 in the two phase region, the sample is stirred with a piece of steel 2 cms. in length and 1.5 mm. in diameter. This piece of steel is drawn up and down inside the tube by means of electromagnet (E). The magnet is wound on a hollow brass magnet form from

1600 turns of 22 gage, double cotton-covered magnet wire, and carries a current of 3.5 amperes.

The magnet is suspended from two lengths of 200 pound test nylon leader which runs up over two pairs of pulleys (not shown) then down to a rotating wheel driven through a 32:1 reducing gear by a 1800 RPM motor. One complete cycle is made in about one second.

D. PURIFICATION OF MATERIALS

(1) The Generation and Purification of Nitrogen.

(a) Apparatus.

Because commercial tank nitrogen contains significant quantities of the unreactive gases such as argon, it cannot be purified with chemical reagents. However, nitrogen chemically produced is capable of fairly easy chemical purification by absorption of impurities from it in a gas purification train.

An excellent way in which nitrogen can be thus generated and purified is that of Smith and Taylor (31) and a modification of their apparatus was used and is shown in Fig. III.

The nitrogen is produced in flask (A) from the reaction of saturated KNO_2 with saturated $(\text{NH}_4)_2\text{SO}_4$, dropping funnel (B) containing the KNO_2 . Mercury reservoir (C) serves to relieve excess pressure.

Nitrogen passes first into scrubber (D) which contains a solution to absorb the oxides of nitrogen. The solution has the following composition (32):

15% anhydrous FeSO_4

15% H_2SO_4 (64%)

70% water

Although Smith and Taylor did not use a reagent to remove the oxides of nitrogen, it was noticed that they were produced in perceptible quantities and provision was made for their removal as it was in a similar apparatus (33).

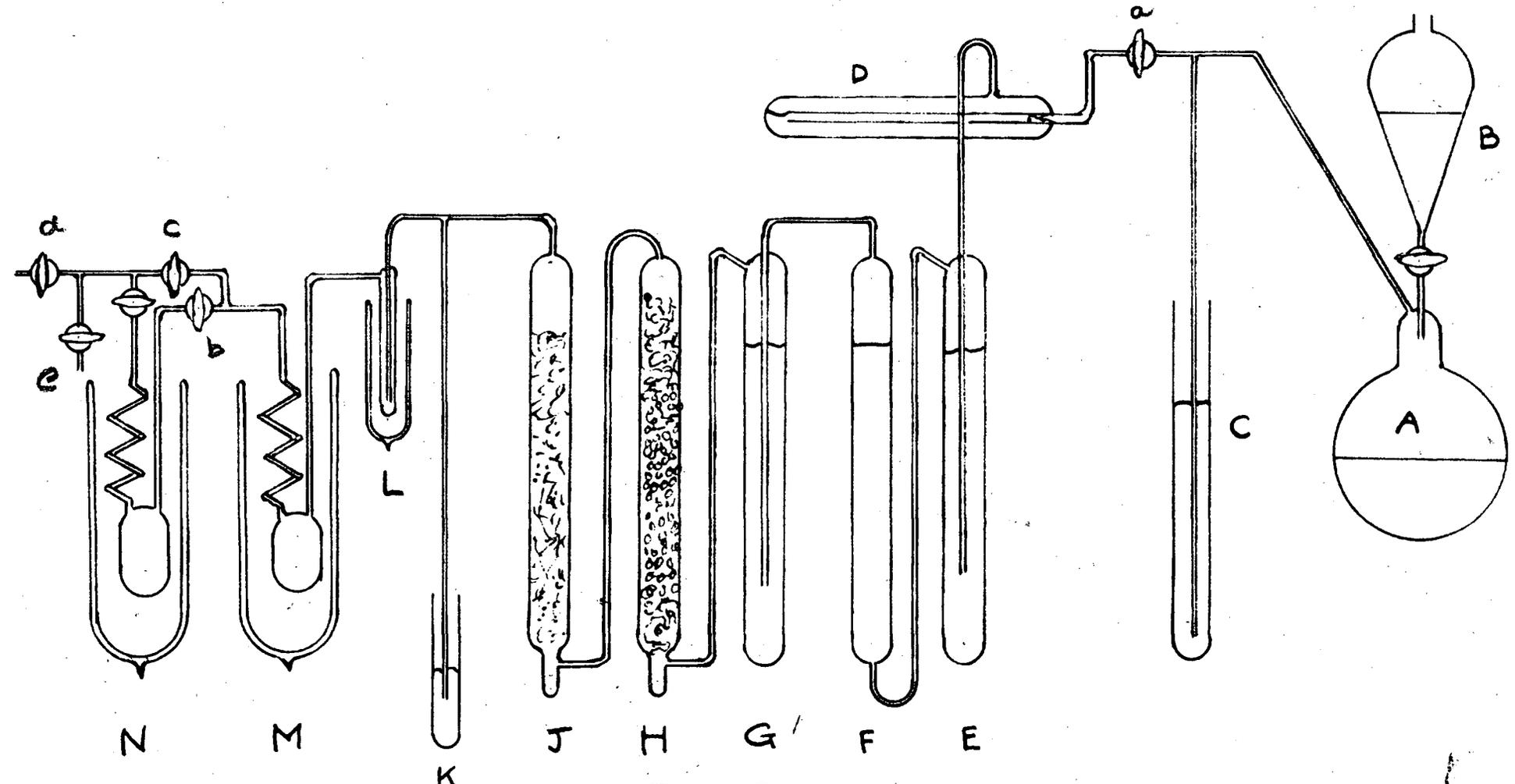


Fig. 3

NITROGEN GENERATION AND PURIFICATION TRAIN

From this scrubber the nitrogen passes into a bottle containing Fieser's solution (34), an oxygen absorbent having the following composition:

$\text{Na}_2\text{S}_2\text{O}_4$ (86.7%)	16 gm.
NaOH (stick)	13.3 gm.
Anthraquinone-B-sulfonate (95%)	4 gm.
H_2O	100 gm.

This solution, is not only a more efficient absorbent than pyrogallol but does not give off undesirable by-products such as CO_2 . Further, the solution is blood red when freshly compounded and brown when spent.

The nitrogen next passes into a solution of concentrated H_2SO_4 , F, which absorbs the bulk of the water vapor present, and then through 10% NaOH , G, which absorbs CO_2 and further moisture. Remaining quantities of water are removed in bottle H, containing KOH pellets, and bottle J, containing P_2O_5 .

Mercury reservoir K serves to relieve excess pressure.

Liquid air trap L cools the nitrogen before it enters distillation stage M and N.

In the final stage nitrogen is first condensed in the reservoir at M. This is accomplished by bubbling tank hydrogen into commercial liquid nitrogen contained in the Dewar flask surrounding the reservoir, and by keeping the pressure in the reservoir three to four inches of mercury

above atmospheric pressure by raising mercury reservoir K.

Next the nitrogen is gently boiled and the vapors allowed to escape to the atmosphere for a few minutes. The middle fraction is then distilled into bulb N, and the residue is boiled off to the atmosphere.

(b) Procedure.

Heat is supplied to flask A by means of a 250 watt heat lamp controlled by a variac.

With valve (a) closed KNO_2 is allowed to drop slowly from the funnel until nitrogen bubbles out through the mercury at C. At this point (a) is carefully opened to allow passage of nitrogen through the train. After the nitrogen bubbles out at K, the distillation procedure begins.

Hydrogen is first allowed to bubble into flask M containing liquid nitrogen, while (b) remains closed. When about 50 ml. of liquid nitrogen has accumulated, the hydrogen is passed through N, and M is slowly lowered. With (b) closed and (e) and (c) open, the first 5 ml. is let out to the atmosphere. Then (e) and (c) are closed and (b) opened. The middle fraction is boiled over to N and finally the last 5 ml. are let out into the atmosphere.

It was noticed that the liquid in M had a bluish cast and upon closer inspection, it was found that the bottom of the reservoir was lined with a blue solid. This solid vaporized into a brown gas when the final portion of the nitrogen was let to the atmosphere. The gas was obviously NO_2 .

An inspection of the scrubber bottle D showed that the solution was dark brown in color where previously it had been light green. The solution had obviously become saturated and the oxides had been carried through the train.

Upon all subsequent distillations it was noticed that the liquid in the reservoir was water-white indicating that the distillation procedure had been effective in eliminating the colored impurity.

The liquid was stored in reservoir N until it was used to fill the capillaries.

(2) The Purification of Mercury.

Mercury with visible scum on the surface was first filtered through a funnel the stem of which was drawn out into a fine capillary. It was then allowed to fall from a similar funnel into a scrubber four feet long containing 10% NaOH, to remove grease. Acid reactive metals and their oxides were next removed in a similar scrubber containing 15% nitric acid. The mercury was finally washed in distilled water.

The water was removed from the mercury by decantation and then by vacuum desiccation.

The mercury was distilled three times in vacuum to remove the heavy metals.

The mercury thus obtained was mirror-like in complexion, had no visible surface impurities, and did not form a scum on the glass container upon prolonged standing.

The mercury was stored in narrow-necked, ground glass stoppered bottles in a dark cupboard.

(3) Purification of Organic Compounds.

(a) Apparatus.

Most of the compounds used were originally C.P. and were distilled once.

The distillation column used was vacuum-jacketted and silvered. It was packed for its two foot length with 1/8 in. pyrex helices, and was equivalent to 13 theoretical plates.

A stopcock on the product line could be adjusted to vary the take-off and reflux. Drip counters were placed on the reflux line and on the product line and the reflux ratio could thus be estimated.

A vacuum adapter was placed on the product line which made it possible to remove the product flask at any time without disturbing the vacuum on the system to any great degree.

Provision was made to hang a thermometer in the path of the ascending vapor.

The stopcock on the product line was lubricated from the outside with apiezon and did not leak perceptibly.

Heat was supplied to the two litre boiling flask by a zipper heating mantle completely enclosing the flask, supplied with current from a variac.

The helices were added to the column one at a time, all incomplete and chained helices being discarded. Only in this manner can the most efficient use be made of the packing.

(b) Procedure.

Most of the compounds used were C.P. and all were fractionated once with the exception of bromonaphthalene.

In an effort to obtain constant pressure distillation two different types of manostat were used but were found unsatisfactory, for they gave too sudden pressure surges. It was decided, therefore, to use a vacuum pump directly for distillation of the high boiling compounds such as methyl salicylate and higher, and to use the aspirator for the rest except carbon disulfide which was distilled at its normal boiling point.

It was noticed that the pressure slowly fell as the distillation proceeded making it impossible to assign a distillation temperature but at the same time not being sudden enough to disturb the equilibrium.

In each distillation, the distillate upon first being condensed was allowed to run into the product bottle. The stopcock was then closed and the column operated at total reflux for one half hour after which the distillate was run to the product bottle at finite reflux ratio.

When approximately 25% of the original charge had been collected, the product bottle was removed, and a clean bottle put in its place. As the distillation proceeded, the reflux ratio was raised to make up for the changing

composition of the material in the boiler.

A brief summary of the conditions of distillation and physical properties of the substances are given below with references. The bracketed indices are taken from the Handbook of Chemistry and Physics.

Carbon disulfide (technical grade) (35, 36)

Pressure: atmospheric
Temperature: 46.0° to 46.1°C.
Properties: water-white

Chlorobenzene (C.P.) (37)

Pressure: 24 mm.
Temperature: 58.0° to 59.0°C.
Properties: $n_D^{20} = 1.5248$ (1.5247), water-white

Bromobenzene (C.P.) (38)

Pressure: 24 mm.
Temperature: 58.0° to 59.0°C.
Properties: $n_D^{20} = 1.5598$ (1.55977)

Aniline (reagent grade) (39 - 42)

Pressure: 6 mm.
Temperature: 62.0° to 63.0°C.
Properties: $n_D^{20} = 1.5864$ (1.5863)
Color: dark red, visible water.
Distilled from zinc dust.

The pure aniline was stored over activated alumina.

Methyl salicylate (U.S.P.)

Pressure: 3 mm.
Temperature: 73° to 76°C.
Properties: $n_D^{20} = 1.5369$ (1.5369) water-white

In each distillation the charge equalled about one litre and the middle 50 to 60% was collected. The reflux ratio went from 4:1 to 6:1.

1-bromonaphthlene (C.P.) was not purified for its

index of refraction agreed with the accepted value of $n_D^{20} = 1.6582$.

The refractive indices were taken by means of an Abbé refractometer calibrated with reference standards. The instrument was maintained within the temperature limits of $\pm 0.1^\circ\text{C}$. by means of circulation from a constant temperature bath.

All the compounds are stable and easily stored, with the exception of aniline which is not only hygroscopic, but unstable in sunlight and air. The aniline was stored in a dark, narrow-necked, ground glass stoppered bottle over activated alumina. The bottle was placed in a dark cupboard.

(4) The Purification of Normal - Butanol.

Although the effect of purity on P - V - T measurements is comparable with its effect on the determination of most physical properties, the accurate determination of the critical temperature and pressure is considerably effected by the purity of the sample. For this reason it was necessary to carry out a careful and thorough purification.

From twenty literature references, seven were chosen as a guide because of their thorough description and the consistency of the physical constants used as a criterion of purity (43 - 49).

The article of Brunel, Crenshaw and Tobin was exceedingly valuable for it discussed several methods the authors tried, and compared the products of each method.

The purification can be broken into two steps; eliminating the organic impurities, and eliminating water. As water is easily picked up from the air, it was decided to remove it last.

Complicated procedures involving contacting the alcohol with several reagents such as sodium hydrogen sulfite, hydrochloric acid, sodium hydroxide, as well as desiccants, as was carried out by Harkins, by Webb, and by Ernst, were discarded in favor of the more straightforward procedure of Brunel et al, involving several fractionations, and contact with desiccants.

The work of Brunel showed that calcium oxide was the best desiccant compared to sodium, barium oxide and calcium. In addition it was decided to use magnesium (which had been used in most of the other references) and activated alumina. Not only does activated alumina absorb water better than phosphorous pentoxide and sulfuric acid, but it absorbs trace organic impurities.

The apparatus and procedure are described below.

(a) Apparatus.

The distillation apparatus consisted of a vacuum-jacketed, silvered, distillation column, packed for its four-foot length with 1/8 in. pyrex helices. Its fractionating power is equivalent to 20 theoretical plates.

Reflux and take-off could be adjusted by means of one stopcock on each of two product lines and use could be

made of both product bottles during a single distillation, one for primary overhead and the other for the main product.

A thermometer reading in tenths of a degree centigrade was suspended in the path of the vapor.

The two-litre boiling flask was heated with a Glascol mantle controlled by a variac.

The still was used only for the purification of normal - butanol to eliminate any probability of contamination.

(b) Procedure.

Two litres of chemically pure butanol, faintly amber in color were distilled at 60 mm. of mercury pressure and one litre collected. The distillate was water-white in color; the residue amber.

The distillate was refluxed with 100 gm. of calcium oxide for eight hours and distilled at atmospheric pressure with a high reflux ratio. The middle 60% was collected.

This was refluxed with two grams of reagent grade magnesium for eight hours and distilled at high reflux at atmospheric pressure. The middle 75% was collected in the range 116.8 - .9°C./750 mm.

The distillate was refluxed for eight hours with activated alumina heated overnight at 175°C. for activation. The temperature of distillation was 117.2°C. and the middle 60%, or 300 c.c. was collected.

The butanol was stored over alumina in the product flask.

The index of refraction at 20°C. was 1.3992, the literature values being 1.3990 (46), 1.39929 (51), 1.3998 (52), 1.3992 (53, 55), 1.3994 (54). The index of refraction at 25°C. was 1.3974, the literature values being 1.3974 (43, 47) and 1.3975 (48, 56).

E. PROCEDURES AND RESULTS

(1) Calibration of the Thick-Walled Capillary Tubes.

The pressure cells bore the trade mark "true-bore" and were the product of the Fischer and Porter Company.

The purpose of the calibration was to determine the internal volume of the capillary between fixed points along its length.

The method consisted of weighing the quantity of pure mercury required to fill the tube between two points whose distance apart was measured with a cathetometer.

To the end of the tube which would be later sealed was attached a straight-bore stopcock, the free arm of which was drawn out to a fine tip. The tube was then clamped in a vertical position with the cock on the bottom. The top of the tube was attached to a vacuum pump.

Before the operation was started, the tube was cleaned by running through it in succession, chromic acid, distilled water, ethyl alcohol, and carbon tetrachloride. The stopcock core was then carefully greased only at its extremities, and not close to the centre. The core was placed in position and worked well in by rotating it. As the grease spread out, carbon tetrachloride was run through the tube and the stopcock rotated quickly. This was repeated several times until there was left only a thin coating of grease at the extremities which did not spread towards the centre upon prolonged turning. The carbon tetrachloride was evaporated with

a stream of tank nitrogen.

The actual calibration was carried out by placing beneath the cock a previously weighed weighing bottle containing about 60 gms. of purified mercury. With the cock closed, the pump was started and then turned off, the cock opened to allow the mercury to rise just above it, the cock closed, and air admitted to above the mercury.

With the cathetometer a reading was taken of the bottom of the meniscus to 0.01 mm., and of the height of the meniscus to .005 mm. by means of the micrometer. The height reading was referred to a glass marker attached to the capillary. The bottle was now weighed and placed beneath the cock, the cock opened to allow the mercury to fall slightly, and the pump turned on until the mercury rose to a new position roughly one centimeter above its former level. The process of drawing the mercury up and weighing the bottle was continued until the mercury level reached the top of the tube.

The volume of the tube from the first level to each higher level was then computed. This was done by determining the net weight of mercury required to fill the tube between the two levels, or the difference in the weight of the bottle when the mercury stood at the lowest level and its weight when the mercury stood at a higher level. The net weight was corrected for air buoyancy.

This net weight of mercury represented the volume occupied between the two levels concerned, plus the volume

occupied by the meniscus at the higher level, minus the volume of the meniscus at the base or first level (a constant amount). To find the true value of the volume of the cylindrical section, the volume occupied by the two menisci were computed from data in the International Critical Tables (50). This data was plotted graphically and the volume corresponding to a given meniscus height was read from the graph.

The volume of mercury was corrected to the temperature recorded by a thermometer placed in the mercury from time to time.

The capillary after being calibrated was sealed off at the end containing the stopcock, and the volume of the tip was determined by pouring through a hairlike tube to the bottom of the capillary, a weighed amount of mercury.

Three determinations were made and the mean taken.

(It is estimated that the absolute volume of all sections ten centimeters or longer is known within 0.1% or less).

(2) Calibration of the Thermel.

The thermel was calibrated in position in the bath against a platinum resistance thermometer the head of which was located directly beneath the thermel. ~~The~~ 2.5 ohm platinum thermometer used - Serial No. 317863 - was calibrated in 1939 by the National Bureau of Standards. It checked at the ice point to within 0.0001 ohm of the value recorded on the N.B.S. certificate.

During calibration the cold junction was submerged in a Dewar flask containing melting ice.

The calibrations were carried out at four widely spaced groups of temperatures; 0°C., 25°C., 140 and 150°, and 190, 200, 210 and 220°C. and a graph was plotted of the deviations of the values from the accepted values given in the Wheelco bulletin (57). The points fell on a smooth curve, the general shape of which is typical of thermel deviations. The deviations in the operating range go from 31 to 38 microvolts, a spread of .14°C.

The temperature of the bath was within the limits of 0.01°C. during all calibrations.

(3) Loading the Capillary with an Air Free Sample of Butanol.

The method was a modification of Young's (6). In Fig. IV the capillary is attached by means of a mercury seal to the neck of a round-bottomed flask containing mercury. A small test-tube containing the sample of butanol is attached by means of a standard taper joint to a tube sealed to the

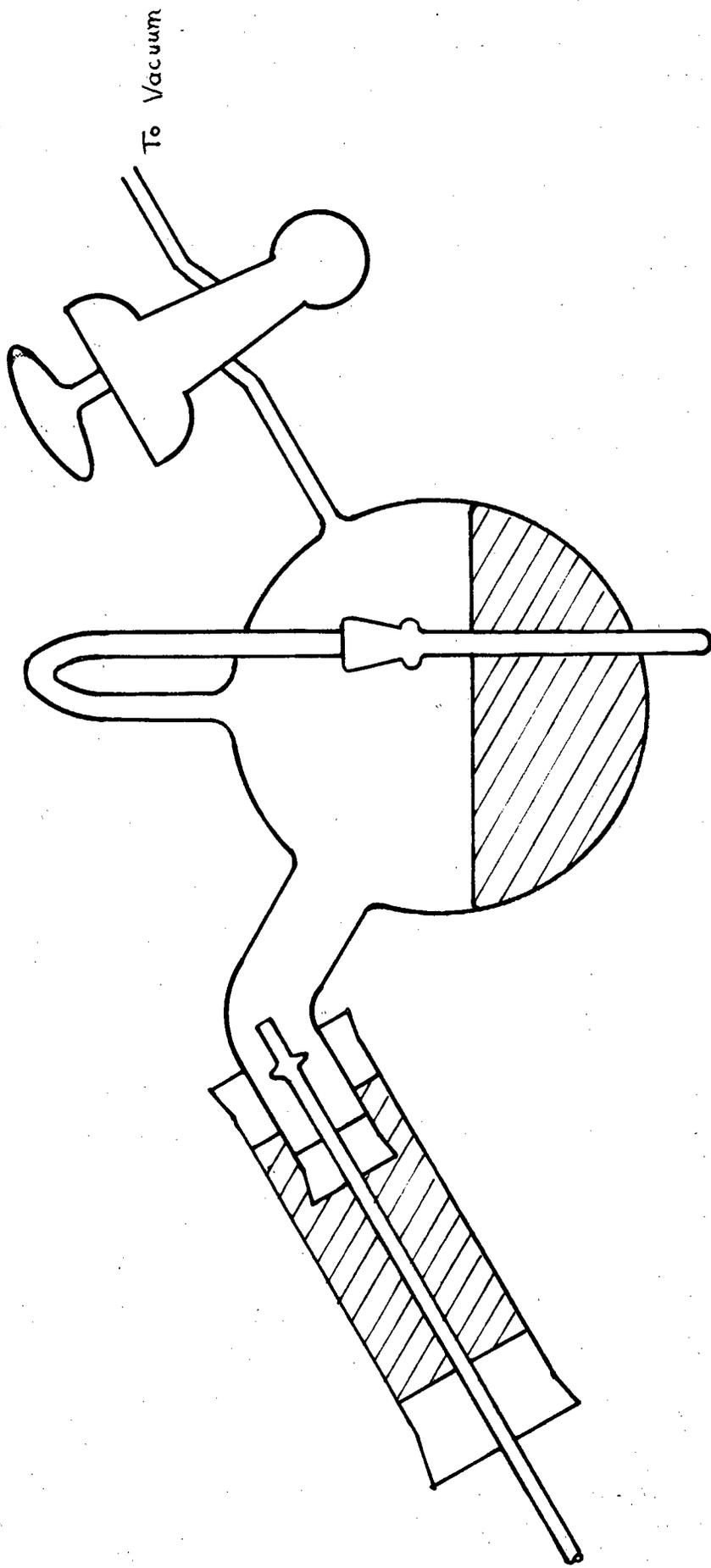


Fig. 4

CAPILARY FILLING DEVICE

top of the flask.

To fill the capillary with the butanol, the flask was first clamped with the bent part of the neck in a vertical position pointing downward. The capillary, which contained the previously cleaned and polished hard steel stirrer, was put in place and the mercury seal assembled. Clean mercury was then poured through the stopcock and the cock greased with apiezon. The flask was joined to a high vacuum line and with the small test tube in place, evacuated at 10^{-4} mm. for eight hours. The tube was then removed, filled with butanol, and replaced. Evacuation was continued and large bubbles could be seen rising from the butanol for about ten minutes, after which no bubbles were seen to rise even though the butanol was at its boiling point. This indicated that surface evacuation was taking place and that the sample was air free.

A Dewar tube full of dry ice was next placed at the tip of the capillary and the butanol allowed to distil over. After a small amount had accumulated, evacuation was continued while the dry ice was removed. In this way it was hoped to remove any last traces of air.

Finally the dry ice was replaced and the butanol distilled over, it taking about two days to accumulate two inches of the sample. During this time the cock was opened frequently to sweep out the flask.

The fact that the filling apparatus was air-tight was indicated when the cock was closed overnight, for upon reopening the cock, no perceptible sound could be heard from

the pump.

The mercury was spilled into the capillary by tipping the apparatus, and air was allowed in.

The tube was then loaded into the compressor.

(4) Loading the Capillaries with Pure Nitrogen.

Previously purified nitrogen (see Purification of Nitrogen) was used to fill the capillary employing a similar apparatus as that used to load the butanol capillary. This apparatus was attached to the end of the nitrogen train and before nitrogen was finally admitted, the capillary was alternatively evacuated and filled with nitrogen until all gases were purged out.

At this point the mercury was spilled into the capillary and the apparatus dismantled. The open end of the tube was placed in a beaker of mercury and in order to fill the reservoir with nitrogen, a fine, hairlike tube was inserted into the capillary beneath the level of the mercury, and nitrogen admitted from the purification train.

The tube was then loaded into the compressor block.

F. SUMMARY AND RECOMMENDATIONS

The compression apparatus has been constructed as described and illustrated, and all the auxiliary apparatus has been found successful in operation.

One high pressure tube has been filled with normal - butanol, as described, and another tube has been filled with nitrogen generated and purified in the purification train. However, it has been shown that the method of packing is as yet unsatisfactory, for breakage of the capillaries occurred as they were being secured in position.

The compounds for use in the constant temperature bath have been adequately purified; the criterion being that they worked satisfactorily in providing a constant temperature. The bath itself has proved successful in operation, for the thermel was adequately calibrated, and the degree of control provided by the bath was shown by the platinum resistance thermometer to be constant within the limits of 0.01°C .

The magnetically operated stirrer has been tried and shown to work satisfactorily.

In preparation for actual experimental determinations, normal - butanol has been carefully purified.

The theoretical and practical importance of the data when it is determined has been illustrated.

It is recommended that a dead-weight piston gage be installed and used in the place of the nitrogen piezometers.

Such a gage will eliminate the error in pressure tube calibration, and in using the experimentally determined nitrogen data.

Some minor modification should be made in the packing arrangement in order to prevent future breaking of the pressure cells. The inclusion of more soft rubber washers between the cup and the steel washer seems to be the best way of doing this. Any modification should be first tested on blanks made up for that purpose, before a capillary tube itself is tried.

Once such an adequate arrangement has been made, the apparatus as it stands promises to be fully satisfactory for the determinations planned.

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