SOME MEASUREMENTS OF THE CONDUCTIVITIES OF DILUTE POTASSIUM CHLORIDE SOLUTIONS

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Philosophy

By
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SUMMARY

1) A constant temperature room has been constructed in which the thermoregulator is controlled by a temperature-sensitive resistance.

2) A thermostat has been constructed in which the temperature is controlled to within 0.001°C.

3) A precision conductance bridge has been built in a very convenient form. Improvements include the replacement of the telephone as null detector by a cathode ray oscilloscope, and the use of a resistance-capacity phase-shift oscillator, which gives a good wave-form.

4) An automatic recycling conductance water still has been built which regularly gives water with a conductivity less than 0.09 micromhos per cm.

5) The conductivities of dilute KCl solutions have been measured, taking special care to prevent errors due to the adsorption of KCl on the surface of glass. Two cells were used for these measurements: a modified Jones cell, and a special conductimetric titration cell.

6) The modified Jones cell has given results in good agreement with the generally-accepted values.

7) The results of the conductimetric titration cell do not agree well with the generally-accepted values; the greatest difference (for the most dilute solution) is 0.4%. The reason for this is not known.

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PART I

CONSTRUCTION OF THE APPARATUS

A. INTRODUCTION

The precision conductance bridge, constant temperature room and thermostat described in this section are similar to those built by Gledhill (1); they were built because it was found that one conductance bridge was not sufficient for the expanding needs of the Chemistry Department.

No attempt has been made to improve on the accuracy claimed by Gledhill, as it is felt that this is at present sufficient for all conductance measurements. However, as regards ease of operation the new apparatus is superior.

B. THE CONSTANT TEMPERATURE ROOM

The control of room temperature in conductance work seems to be the exception rather than the rule. Davies (2) mentions a "small room maintained at a constant temperature about 1°C lower than that of the thermostat, by thermostatically controlled heating coils"; but this the only reference to a constant temperature room (hereafter abbreviated to c-t room) the author has seen in papers on conductance measurements.

The majority of conductance measurements are made at 25°C. In Grahamstown the temperature outside often rises to 30°C in summer, and even in a cool room will go above 25°C; under these conditions some form of cooling is necessary. Direct cooling of the thermostat, either by the addition of ice or by the use of cooling coils, makes accurate temperature control more difficult; it is more satisfactory to insulate the walls of the room and cool the air. If this is done, the thermostat temperature can be kept constant by using heating coils controlled by an "on-off" relay.

Once such a room has been built, there are various reasons for keeping it at a constant temperature:

(i). For accurate work the bridge resistances should be kept at a constant temperature. Some workers (e.g. Shedlovsky (3)) have done this by immersing the large bridge resistances in the same thermostat as the cell; in a c-t room this is unnecessary, and the bridge can be built as a self-contained unit independent of the thermostat.

(ii). It is easier to control the temperature of a thermostat accurately when the room temperature is kept constant at a slightly lower value.

(iii). In carrying out a conductimetric titration, if the temperature of the thermostat differs widely from that of the small amounts of solution added to the cell, there must be a pause after each addition to allow the contents of the cell to attain thermal equilibrium with the thermostat. This is not necessary if the temperature difference is small.

(Note: If a weight burette is to be used for making additions to the cell, as is necessary in accurate work, the balance on which it is weighed should be kept in the c-t room.)

(iv). A c-t room is useful for many physical measurements where the temperature must be kept constant, but need not be accurately controlled.

For these reasons it was decided to build a c-t room in which the temperature could be maintained at 24°C to within 0.1°C.

Site of the c-t room

The "outer room", which houses the c-t room, is a large room on the ground floor of the Chemistry Department. Its use for this purpose is particularly suitable for two reasons:

(i). On all sides except the East it is insulated from the outside by the main part of the building; on the East side it is protected from the sun's rays by a covered sidewalk, except for a short period in the early morning. Because of this, the room remains relatively cool in summer, thus diminishing the load on the cooling plant; and the temperature does not fluctuate much over a period of 24 hours, so that the heating required for the c-t room needs to be readjusted only occasionally.

(ii). Provided the door is kept closed (which is done automatically by a door-closing device), all the air for the c-t room is drawn through the window on the East side. As none of the exhaust fans of the main laboratories discharge on this side, the c-t room is entirely protected from any acid fumes which may be circulating in the building. This is of great value in protecting the delicate apparatus from corrosion.

Construction of the c-t room

The room is very similar to that built by Gledhill and Thomas in 1941. It is 11' 6" long, 9' 4" wide and 6' 5" high, the width being chosen so that the East, West and South walls and the ceiling touch the corresponding parts of the outer room. The floor is 5' 4" above the floor of the outer room; the intervening space makes a convenient storeroom for conductance apparatus.

The walls and ceiling of the c-t room are made of a wooden framework covered with celotex, and are 4" and 3" thick respectively; the floor is made of a similar framework 6" thick, which is covered on the top with wooden flooring boards and on the bottom with celotex. The empty space in the framework is filled with sawdust, which is a cheap and effective insulating material.

Fresh air is brought into the room by means of a ventilation fan of the usual type (9" diameter, displacement roughly 250 c.f.p.m.) in the North wall. The air leaves the room through an opening in the South side of the West wall. The temperature of the incoming air is controlled as described later, thus regulating the temperature of the room.

Arrangement of the fixtures in the room (See Fig. I)

Work done in the Gledhill-Thomas c-t room has shown that it would have been more convenient if more space had been left for the bridge and thermostats; for this reason it was decided to use the whole of the South wall for these units in the new room.

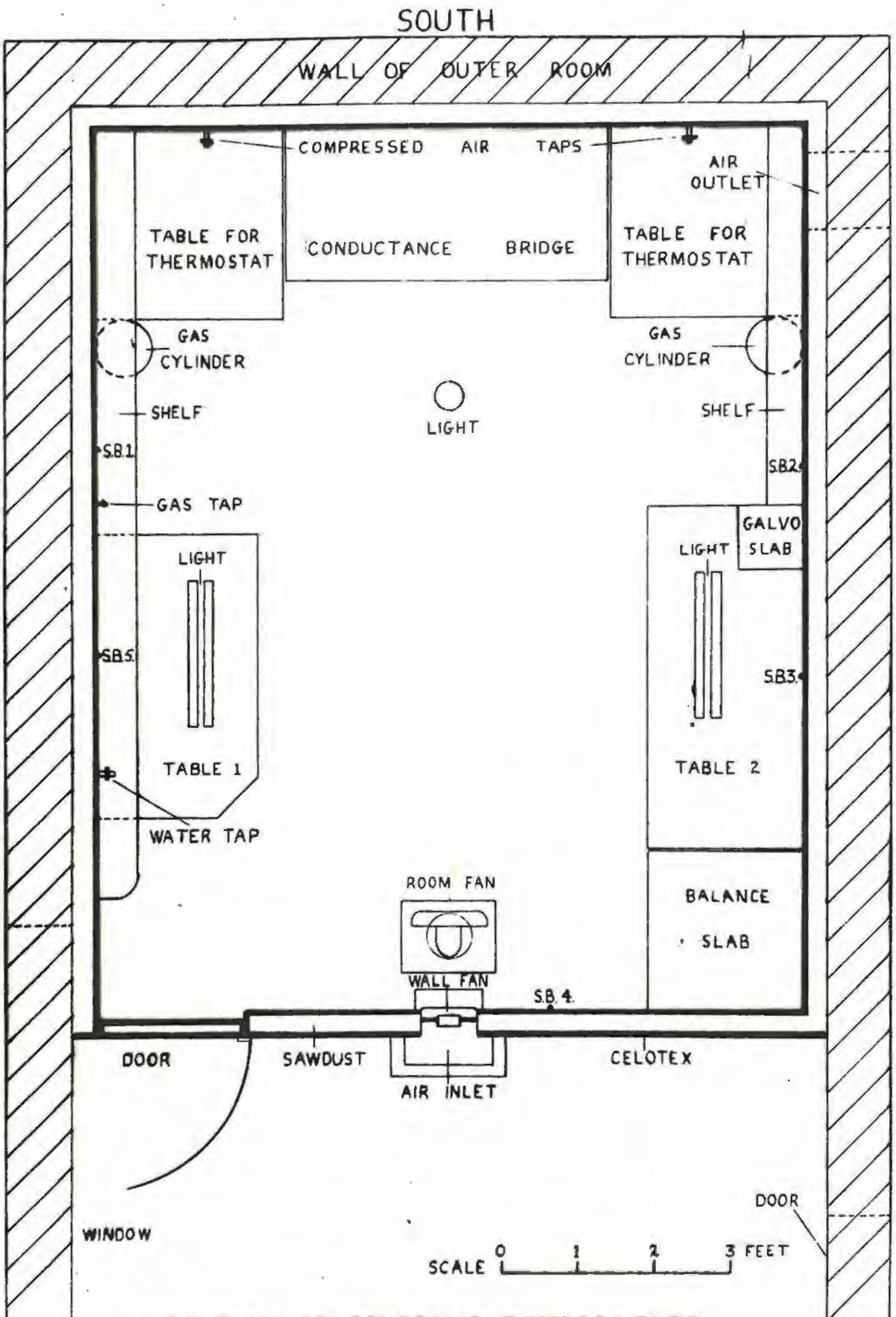

FIG.1 PLAN OF CONSTANT-TEMPERATURE ROOM

The balance and galvanometer slabs are slate slabs which are mounted directly on the brick wall, in order to minimize vibration; they are respectively 3' and 5' above the floor.

As it is occasionally necessary to use a gas other than air in the purification trains, the shelves have been arranged so that it is possible to clamp a gas cylinder vertically next to the thermostat tables.

Room lighting and power

In order to cut down the amount of heat generated in the room, the main illumination is provided by fluorescent lamps, which are a very efficient source of light. However, this type of lamp has the disadvantage that it does not light up instantaneously, and therefore an ordinary filament type lamp has been installed in addition, chiefly for the use of anyone entering the room for only a brief period.

Power to the room is supplied on five switchboards, which are installed as shown in Fig. I. These boards are all fitted with 15 amp-3 prong plugs, which have been wired so that the left-hand pin is neutral, as in certain cases (e.g. thermostat relays) it is necessary to know the polarity. In addition switchboard 3 is fitted with a variety of plugs, in case any piece of apparatus brought into the c-t room is not fitted with a 15 amp-3 prong plug.

Provision has also been made on switchboards 3 and 5 for direct current; any voltage up to 35 v. can be tapped off from a switchboard mounted in the outer room.

Note on the construction of the room

After the c-t room was completed, two disadvantages of building it above floor level became apparent:-

(i). In spite of mounting the balance slab directly on the brick wall, vibration (e.g. caused by people walking along the corridor outside the West wall) affects the balance slightly.

(ii). It is very inconvenient to climb a steep flight of stairs in order to get into the c-t room; this is especially noticeable when one is carrying a large piece of apparatus.

These faults could have been obviated by building the c-t room on the concrete floor of the outer room. The store would then have been above the c-t room, which would have been inconvenient, but less so than the present arrangement.

C. CONTROL OF ROOM TEMPERATURE

Fresh air is supplied to the room by the 9" diameter fan in the North wall, which draws the air through a duct outside the room containing the heating elements and cooling coils. The former are mounted above the latter, as water (condensed from the atmosphere) drips continually from the cooling coils when they are operating. This water is collected by a metal tray mounted below the duct; the tray is fitted with an outlet pipe leading to the drains.

The cooling coils are used only in hot weather, when they operate continuously. The room temperature is regulated by controlling the power to the heating elements.

The Cooling Plant

The cooling plant consists of a twin-cylinder Mills compressor driven by a 2 h.p. 3 phase Delco electric motor; the unit serves both the new and the old c-t rooms, and is mounted in the basement between them. The control switch for the motor is on the switchboard beneath the new c-t room. In addition there used to be a relay controlled by a Siebert-Kuhn thermoregulator in series with the pressure cut-out switch fitted to the compressor, which switched on the unit when the temperature reached a preselected value; however, this is no longer used. While it is theoretically desirable, in practice there is always ample warning of the approach of hot weather, so that it is less trouble to switch on the unit than it is to attend to the battery of the relay. In any case fully automatic control is not practical, as it is desirable to pump down the gas when the unit is to be out of action for any length of time.

The room heater

The main heater consists of two 1000 watt oven elements connected to a three-heat switch, current to which is controlled by the room relay; the power dissipated by these two elements is 500, 1000 or 2000 watts, depending on the setting of the three-heat switch. In addition there is a subsidiary 500 watt "permanent heater" controlled by an ordinary switch, for use in very cold weather. The heaters are wound on grooved porcelain strips, which are mounted on each side of the air duct.

Shortly after the room was put into operation for the first time, it was found that on a very cold night 2500 watts was insufficient to keep the temperature up. Investigation showed this to be due to a current of cold air blowing through the gap beneath the door; when this was closed by attaching a flat piece of rubber to the bottom of the door, no further trouble was experienced. In fact, it is only in quite exceptionally cold weather that it is necessary to use more than 1500 watts.

Circulation of air

When the c-t room was built, the air inlet was covered by a baffle which deflected the air downwards onto a 12" oscillating fan, as shown in Plate I. Later the wall fan broke down, and was replaced by a new type which made it impossible to use the baffle; but this has had little effect on the accuracy of temperature control. The oscillating fan circulates the incoming air to all points in the room, and the air leaves the room via the outlet in the West wall (see Plate II).

Choice of relay

The Struthers-Dunn relays used by Gledhill, although reasonably satisfactory, have two disadvantages:

(i). Unless carefully adjusted, they are inclined to "chatter".

(ii). They are noisy in operation.

As a better relay, viz. the Sunvic type F 102-4 was available, it was decided this instead: a circuit diagram is shown in Fig. V(B). This relay is unusual in that the contacts operate in a high vacuum, thus eliminating all sparking; they can therefore be made much smaller than in a normal relay. The position of the moving contact is controlled by a coil of thin steel wire. When a current (about 25 mA) flows through the wire, it heats up and expands, allowing the contacts to touch; when the current

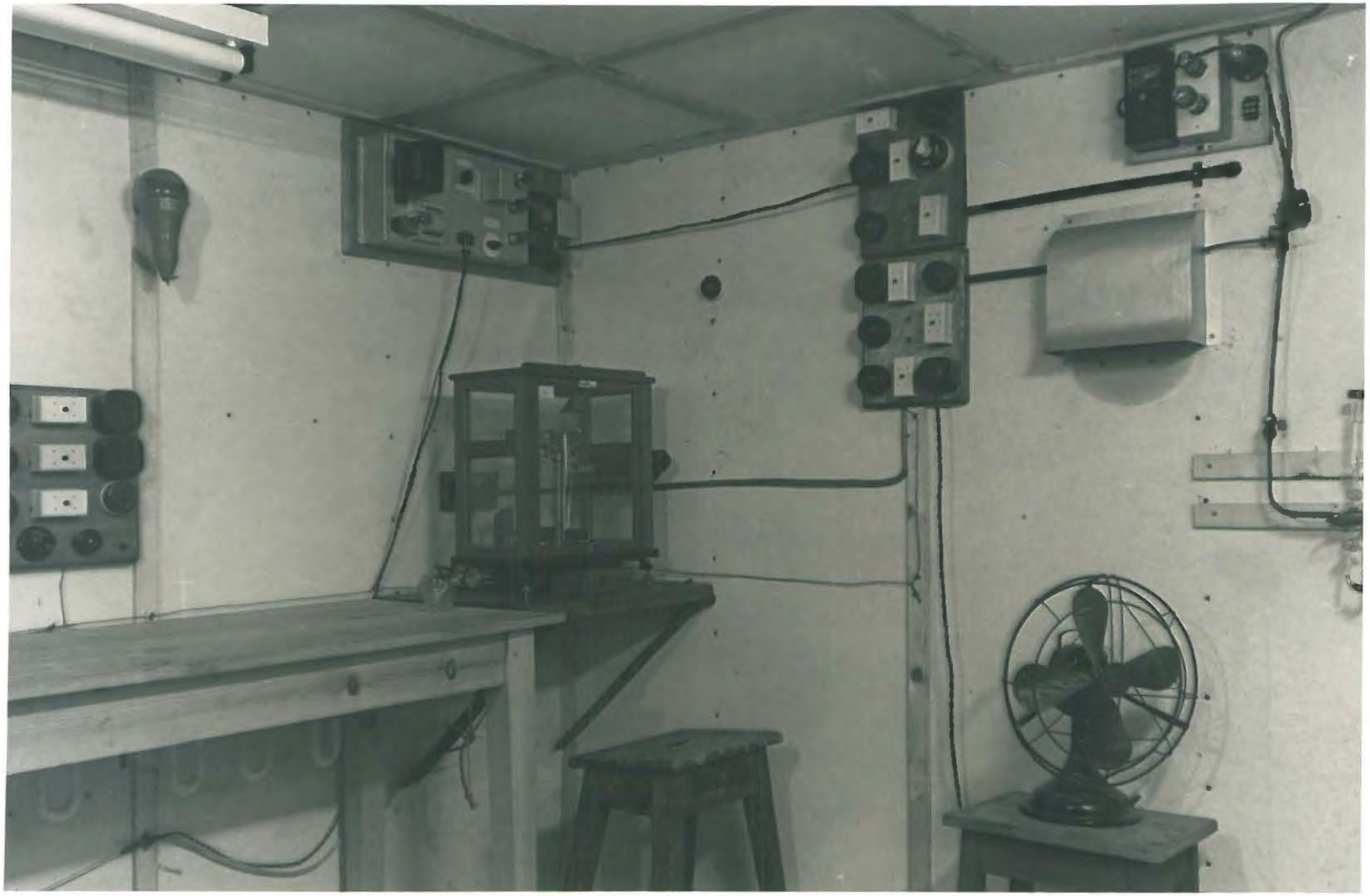

PLATE I

is switched off (or decreased below a critical value) the wire cools down and contracts, thus separating the contacts. As there is a time lag of about two seconds between the flow of control current and the operation of the relay, in normal operation there is little likelihood of chatter, and the relay operates noiselessly. Sunvics have been used for both room and thermostat temperature control, and during four years of operation have never given trouble. At a conservative estimate the room relay has operated over one million times during this period, so it can be seen that the Sunvic is a relay of exceptional quality.

The paraffin thermoregulator

This is similar to the one described by Gledhill (loc. cit.), and was the first to be used in the new c-t room. It consists of a 30 ft. length of $\frac{1}{4}$ inch copper tubing (the main tube) which is fixed to the walls and ceiling of the room; this is joined by a T-union to a 1 ft. length of tubing (the auxiliary tube) which is mounted in the air stream from the wall fan. One end of the main tube is joined to the contactor which controls the relay; the other open ends are closed with screw caps after the tubes have been filled with paraffin.

Although this type of regulator has been used for years in the old c-t room, it was not very satisfactory in the new one. The main reasons for this are:

(i). Some difficulty was experienced in removing all the air bubbles when filling the tubes with paraffin. If this is not done, then changes in barometric pressure will affect the room temperature.

(ii). A great deal of time was spent in locating a leak in the regulator (the symptom of this is a steady rise in room temperature). It was eventually traced to one of the taps in the contactor which had a tendency to work loose in the barrel.

(iii). The most serious trouble was that when someone entered the room the temperature rose by 0.2°C. This can be explained as follows: an adult human being dissipates a considerable amount of heat (more than 100 watts), so that when someone enters the room the amount of <u>external</u> heat required to keep the temperature constant decreases. There will consequently be a brief period of readjustment to the changed conditions, after which the average temperature of the incoming air and the paraffin in the auxiliary tube will be lower than it was originally, and that of the paraffin in the main tube will be higher. While at first sight this implies a rise in the room temperature, it must be remembered that the heat radiated by a person will cause objects near him to be at a higher temperature than the surrounding air. In the ideal case the radiant heat warms the main tube by just the right amount, and the temperature of the room does not alter. This condition is nearly fulfilled in the old c-t room, where the temperature rises for a brief period and falls as soon as sufficient radiant heat has been absorbed. In the new room there was not sufficient compensation, and the temperature rose slightly. This defect could be remedied by adjusting the relative lengths of the main and auxiliary tubes. (It could also be remedied by removing the auxiliary tube and placing the main tube in such a position that it would not be affected by radiation from people in the room; but this solution is not satisfactory, owing to the slow response of the large mass of paraffin to small changes in air temperature.)

Experience with the regulator in the old c-t room has shown that air bubbles tend to form in the paraffin; also the mercury in the contactor tends to become dirty after a few months, in spite of the use of a thermionic relay. This necessitates dismantling and refilling the regulator, which is a troublesome task.

At this stage it was found that there is another method of temperature control depending on a totally different principle, viz. the variation of resistance with temperature. It was therefore decided to stop work on the paraffin regulator, and to build a new one using this principle.

The electronic thermoregulator

To understand the principle of operation of the thermoregulator, a knowledge of the characteristics of the thyratron is necessary. In normal electron tubes, the gas density is so low that the probability of collision of electrons with gas molecules is small and relatively few ions are present. In its simplest form, the thyratron is a triode with a comparatively high gas density, in which the probability of ionizing collisions of electrons with molecules is very high, and many ions are consequently present in the gas. The characteristics of such a tube differ markedly from those of the normal triode (See e.g. Reich (4)).

If one starts with a grid potential considerably more negative than the cut-off value, and then gradually reduces this negative bias, it is found that at the point where the plate current would just start to flow if the tube contained no gas, the plate current suddenly jumps from zero to a very high value; this readily reaches the full emission of the cathode with anode voltages as low as 15 to 20. After the flow of plate current has once started, the control grid has no further effect, and the grid can be made much more negative than cut-off without altering the plate current appreciably. To stop the plate current, one must reduce the plate voltage below the ionizing potential of the gas in the tube.

If alternating voltages are applied to the plate and grid of a thyratron which requires a small positive grid bias to initiate the discharge, the tube will conduct on the positive half-cycle if the voltages are in phase (See Fig.II(B.1.)). If, however, the grid voltage is 180° out of phase with the plate voltage, the tube will not conduct at all (Fig.II(B.2)). The fraction of the cycle for which the tube conducts can be varied between these two limits by suitable adjustment of the phase of the grid voltage; e.g., if the voltage is 90° out of phase, the tube will conduct for approximately $\frac{1}{4}$ cycle (Fig.II(B.3)).

It can easily be shown that, in an a.c. Wheatstone bridge consisting of pure resistances, the output voltage undergoes a phase change of 180° when the bridge passes through balance. If this voltage is suitably amplified and applied to the grid of a thyratron, the phase can be arranged so that the tube will conduct on one side of the balance point and not on the other. This is the principle of operation of the electronic thermoregulator; the variation about the balance point is made dependent on the temperature by making one of the bridge resistances sensitive to temperature changes, and the thyratron current is used to operate a Sunvic relay.

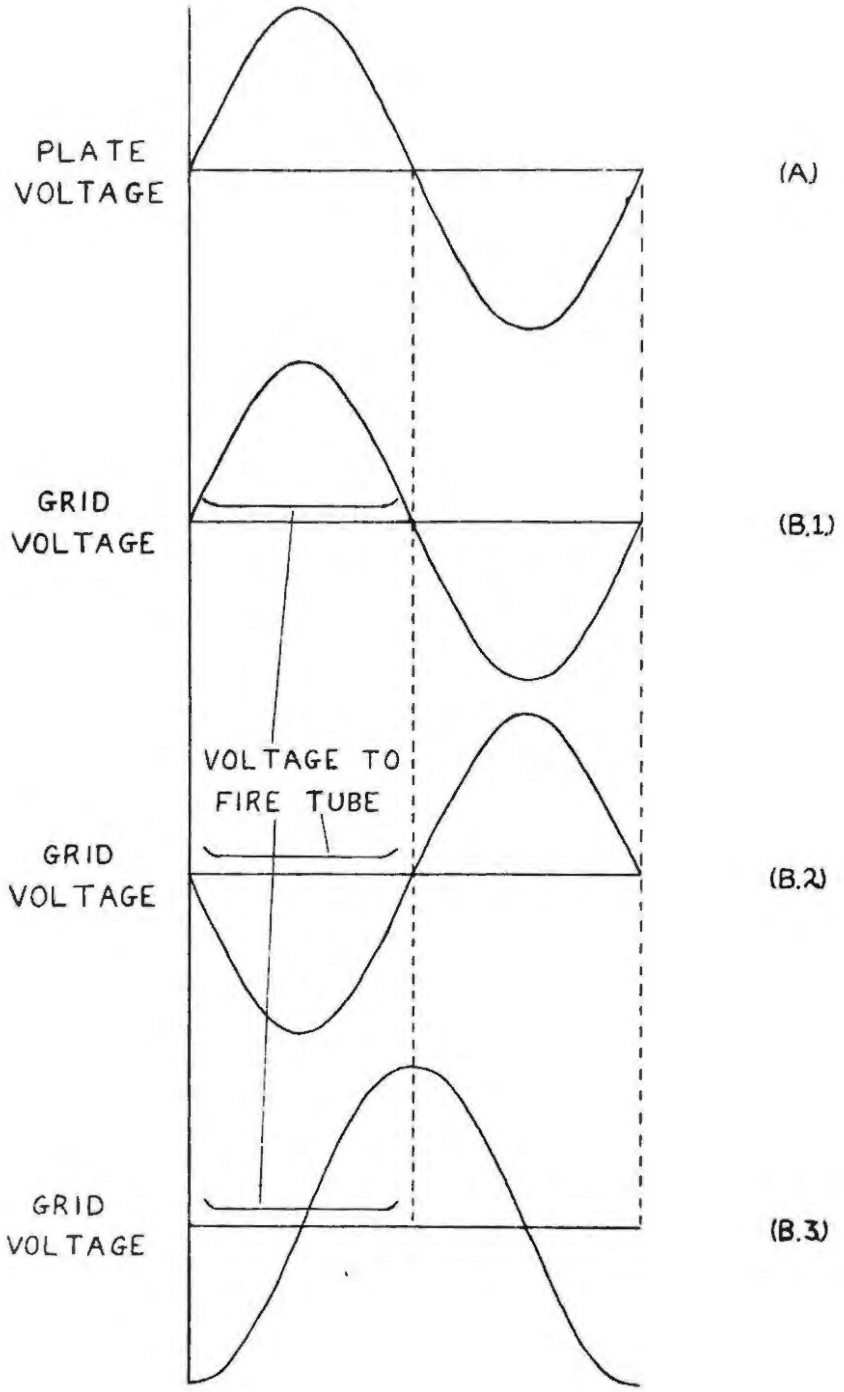

FIG.II OPERATION OF THYRATRON

The design was adapted from a more complex circuit described by Sturtevant (5). In his circuit a larger thyratron is used, and the current from this is passed directly through the heating coils. Continuous control is achieved by adding a constant voltage, 90° out of phase, to the bridge output. At balance the bridge output is zero, and therefore the phase difference between grid and plate is 90°; when the bridge is slightly out of balance, the phase difference will be slightly less or greater than 90°. The power supplied to the thermostat varies accordingly, the bridge being connected so that when the temperature falls more power is dissipated. This type of control is superior to the "on-off " control of the normal regulator; an equilibrium temperature is soon reached, whereas the on-off type oscillates about a mean temperature. As very accurate control was not required, and because of the difficulty of obtaining a suitable thyratron, it was decided to use the simpler circuit.

In actual fact the simple theory given above is not an accurate description of the working of the thermoregulator. The thyratron used(a 6Q5G) does not require a positive bias on the grid to initiate the discharge; on the contrary, with 250 volts applied to the plate, it requires a large negative bias (about 30v.) to prevent the discharge. (At the equilibrium temperature the bridge will therefore not be balanced, but will be just sufficiently off balance to provide the grid bias necessary to prevent the discharge. It might be thought that this is undesirable, as a change in the line voltage will change the degree of unbalance needed to provide the necessary bias i.e. the temperature of the room will alter. However, this effect is negligibly small.) There are also other stray effects which were ignored e.g. the presence of a.c. pick-up (from tube heaters, etc.), and the fact that the 50 cycle a.c. is not a pure sine wave. It is therefore not surprising that the behaviour predicted by this theory - a sudden jump from zero to full current at the equilibrium temperature - is not achieved in practice; however, by modifying the bridge circuit slightly (as described below), it has been possible to cause a very rapid change in current near the balance temperature, and this is quite satisfactory for controlling a relay of the Sunvic type. This modification is the most successful of several attempts to improve the sharpness of the transition; it was discovered by experiment, and the theory has not been worked out.

The temperature-controlling Wheatstone bridge (Fig. III(A)).

It is essential that the resistors used in this bridge be of good quality, as a change of 0.04% in the resistance of one arm will change the room temperature by 0.1°C.

A material suitable for the temperature sensitive resistor (R_t) is one which has a high temperature coefficient of resistivity; unfortunately this is in general a property of the good conductors only, so that it is necessary to use very fine wire. It was eventually decided to use copper wire, as this was readily available. Sturtevant used a resistance of 200 ohms in each arm of the bridge; the value does not appear to be critical, but it was decided to follow his example. As the finest wire available had a resistance of ½ ohm per foot, a length of 400 feet was required.

The winding of the resistor was complicated by the fact that it had to be non-inductive (as recommended by Sturtevant). There are several types of non-inductive winding (See Hague (6)); the type which was finally used is the bifilar, as this is the least difficult to wind. As the resistor has to be at the average temperature of the room, rather than at the temperature of any particular point, the wire was wound on a 35 foot length of ¼ inch diameter rope, which is sufficiently flexible to be mounted on the wall in any desired position. No machine was available for winding the resistor on the rope former, and this had to be done by hand; it proved to be a very laborious task.

The copper wire was doubled, and the twin thread wound onto the rope, with a separation of about 1/16 inch between strands. It is evident that in a bifilar winding a short circuit between adjacent strands would short out part of the resistor; it was therefore decided not to rely on the enamel insulation of the wire, and great care was taken to prevent two strands from touching. As soon as the winding had been completed, the resistor was coated with shellac to fix the wire in place.

A thin wire responds rapidly to changes in air temperature; therefore it is not necessary to place any part of the resistor in the stream of incoming air (as was the case with the tube of the paraffin regulator). Because no part is in the air stream, it is essential that the resistor should not be heated by radiation from sources of heat in the room; for this reason it was painted with aluminium paint, and was mounted so as to be exposed as little as possible to radiant heat. (The section above the bridge can be seen in Plate II). No attempt was made to adjust the value accurately to 200 ohms, as it was less trouble to wind three resistors of the bridge to approximate values, and then adjust the fourth to the

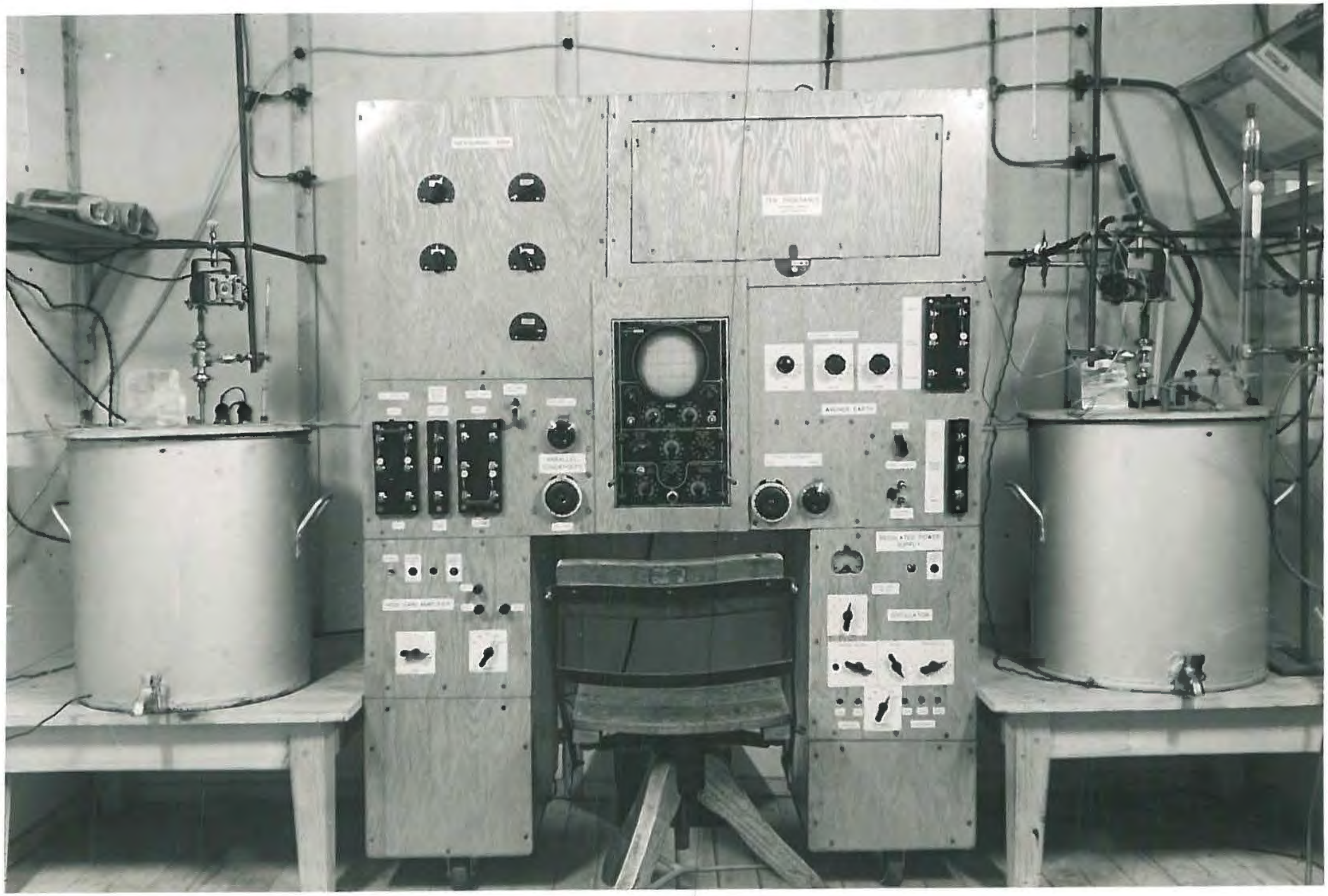
PARALLEL CONDENSERS
HIGH GAIN AMPLIFIER
ANODE EARTH
REGULATED POWER SUPPLY
OSCILLATOR

PLATE II

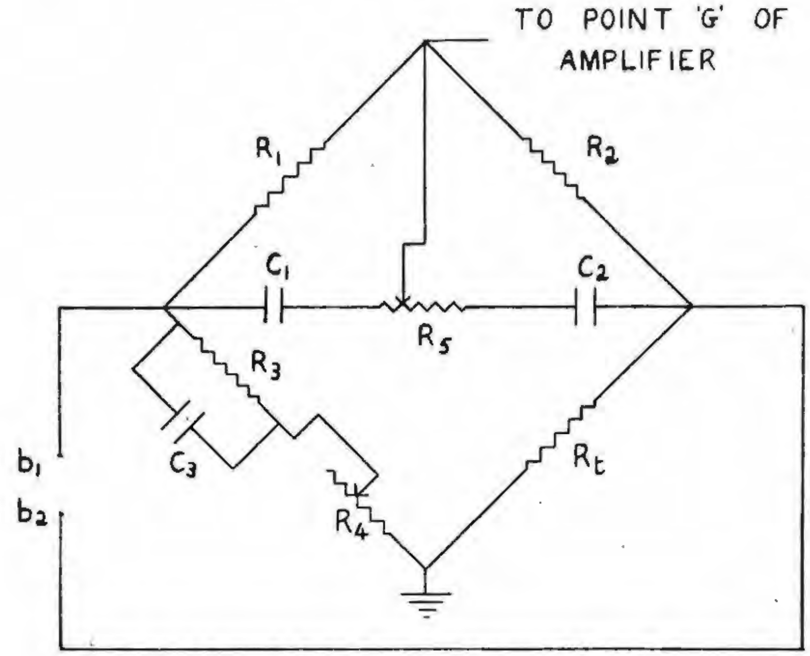

FIG.III(A) RELAY BRIDGE CIRCUIT

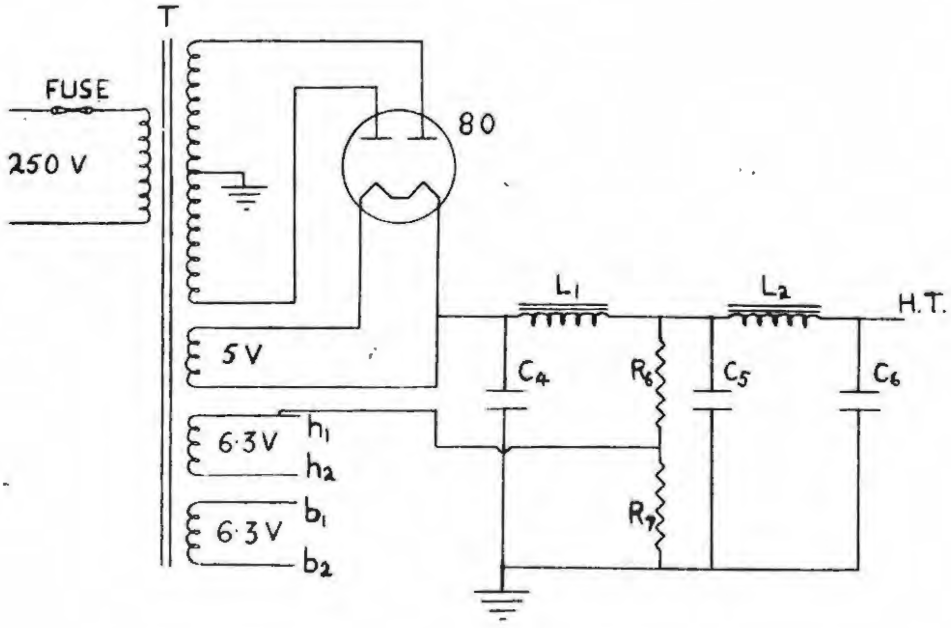

FIG. III (B) RELAY POWER SUPPLY

FIG. III(A). RELAY BRIDGE CIRCUIT

R_1 = 187 ohms
R_2 = 189 ohms
R_3 = 209 ohms
R_4 = 5 ohms
R_5 = 100 K

C_1 = 0.25 μF
C_2 = 0.25 μF
C_3 = 0.20 μF

FIG. III(B). RELAY POWER SUPPLY

R_6 = 250 K
R_7 = 10 K
L_1 = 30 henries
L_2 = 30 henries

C_4 = 8 μF
C_5 = 8 μF
C_6 = 8 μF
T = mains transformer

value required to balance the bridge.

The other three bridge resistors are made of manganin wire, which has a very small temperature coefficient of resistance; the gauge used was such that approximately 15 feet of wire was required for a resistance of 200 ohms. Each resistor is wound non-inductively on an ebonite strip, whose edges are grooved to keep the wire in position. After winding the resistors were waxed to prevent changes in humidity from causing a drift in resistance.

All the bridge components except R_t are mounted in the section of the chassis between the power pack and the amplifier, and are shielded from both by strips of galvanized iron (see Plate III); this arrangement was adopted so that the amplifier could be as far as possible from the transformer in the power pack.

To enable the room temperature to be adjusted, a variable low resistance R_4 (5 ohms maximum) is placed in series with R_3. Condenser C_3 is included to balance out stray capacities to earth in the windings of R_t and the transformer (its value was determined experimentally). C_1, C_2, and R_5 were added to improve the sharpness of the "on-off" control. This part of the circuit is similar to that described by Sturtevant, and is designed to give the component 90° out of phase with the bridge voltage, thus giving continuous control. R_5 is a sensitivity adjustment which, if set too far, changes the continuous control to "on-off" control; and this is the setting which is used in the present case.

The power supply (Fig. III(B))

This is a conventional power pack, fitted with an extra stage of smoothing to eliminate a.c. as far as possible. In the original chassis both L_1 and L_2 were mounted near the mains transformer; however, it was found that magnetic coupling between the chokes and the transformer introduced a small a.c. component into the d.c. supply; this was remedied by mounting L_2 separately, at some distance from the transformer. With this design no a.c. could be detected in the d.c. supply when it was used to replace the batteries in a high-gain amplifier.

The potential divider R_6-R_7 gives the valve heaters a positive bias with respect to the cathode in order to minimize a.c. pick-up.

Amplifier and thyratron (Fig. IV)

V_1 and V_2 constitute a two-stage amplifier with an overall gain of roughly 10,000. The screen grid voltage is maintained at about 100 v. by the potential dividers R_1-R_2 and R_6-R_7, as simple voltage-dropping resistances are not recommended when the h.t. is above 300 volts (7). The cathode resistances were chosen to give a grid bias of 2 to $2\frac{1}{2}$ volts for V_1, and 1 to $1\frac{1}{2}$ volts for V_2. The 50 μF

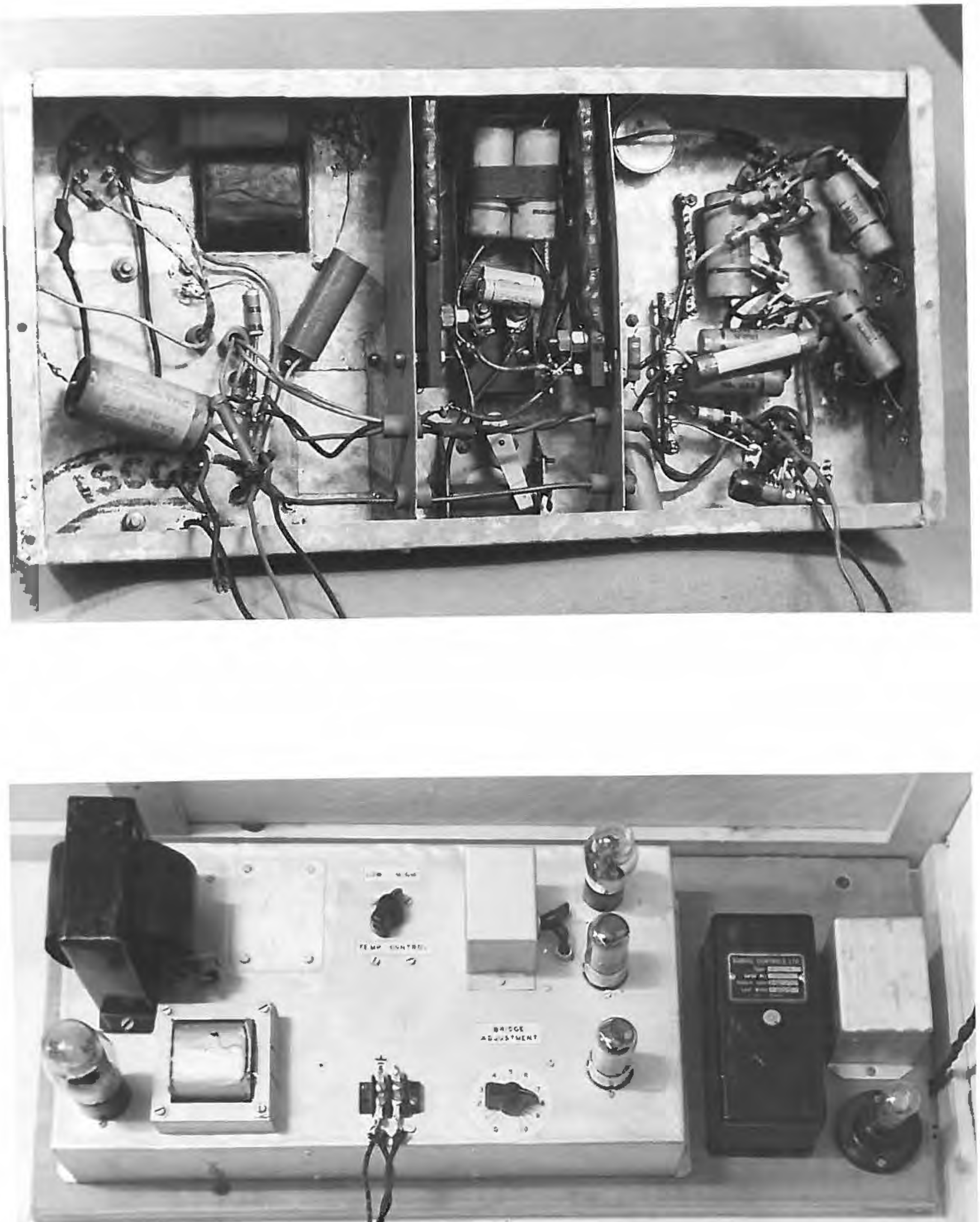

PLATE III

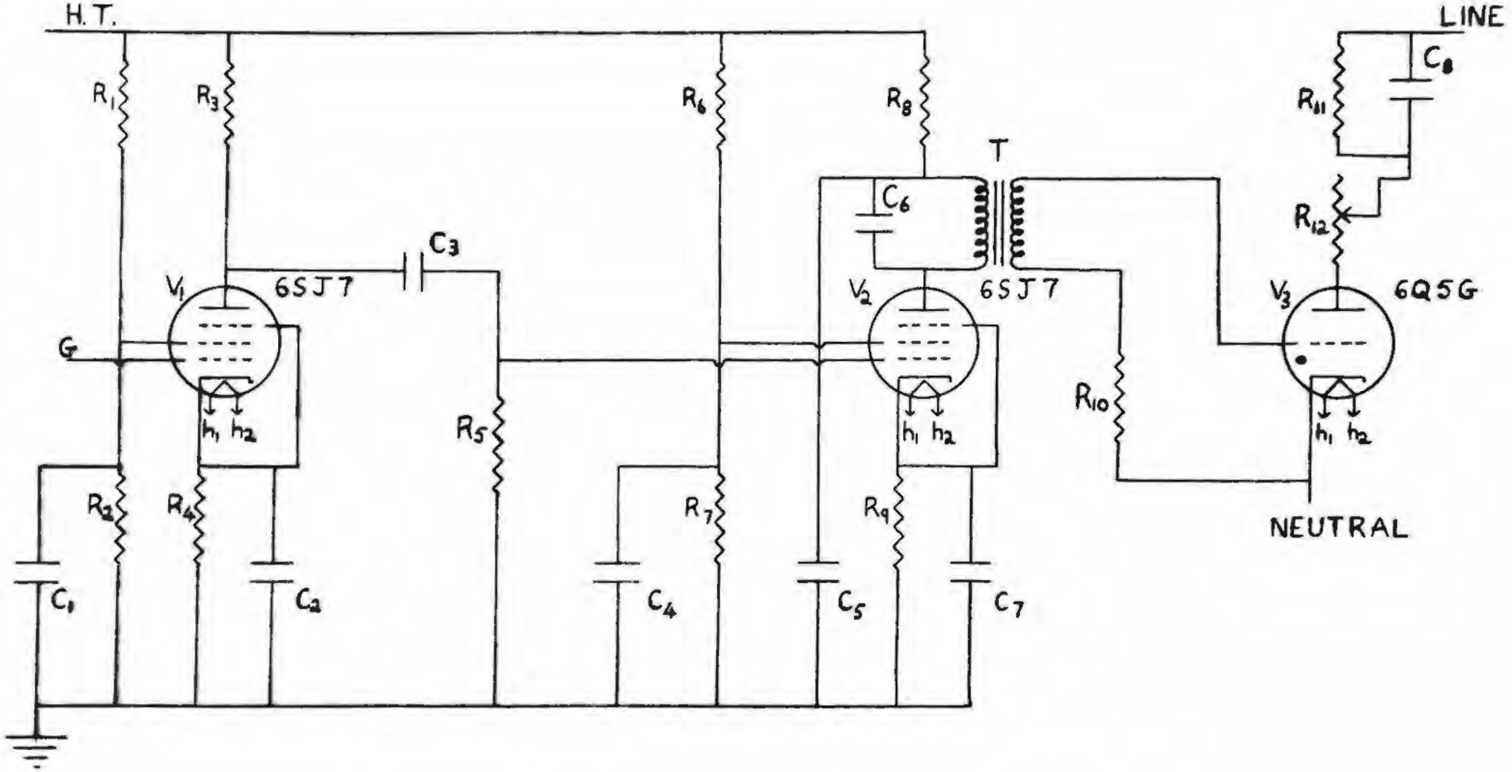

FIG. IV RELAY AMPLIFIER AND THYRATRON

FIG. IV. RELAY AMPLIFIER AND THYRATRON

R_1 = 100 K
R_2 = 50 K
R_3 = 100 K
R_4 = 1 K
R_5 = 1 M
R_6 = 75 K
R_7 = 50 K
R_8 = 25 K
R_9 = 0.5 K
R_{10} = 100 K
R_{11} = Sunvic control element
R_{12} = 10 K, 10 watt variable

C_1 = 0.1 μF
C_2 = 50 μF
C_3 = 0.25 μF
C_4 = 0.1 μF
C_5 = 8 μF
C_6 = 0.2 μF
C_7 = 50 μF
C_8 = 50 μF
T = coupling transformer

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bypass condensers C_2 and C_7 were installed because they were available, but such high values are not really necessary.

Originally the coupling between the output of the amplifier and the thyratron was the conventional resistance-capacity type, but this was abandoned because the relay would not go off sharply, but tended to "chatter" about twenty times before finally operating. The cause of this is almost certainly the small rise in line voltage (about 5 volts) when the heater goes off, but the theory of the effect is obscure. As the effect was greatly diminished by using transformer coupling, it possibly involved charging of the coupling condenser by grid current from V_3.

When the coupling transformer was installed, care was taken to connect it in such a way that the rise in line voltage when the heater goes off gives a negative pulse at the grid of V_3, and not a positive one; this arrangement tends to reduce "chatter". The primary of the transformer is tuned to 50 c.p.s. (the mains frequency), partly to prevent undesired phase changes, and partly to increase the plate load, and hence the amplification in V_2. As there is only a small d.c. voltage drop across it, a voltage-dropping resistor R_8, with decoupling condenser C_5, is necessary. R_{10} is included to limit the grid current of V_3. C_8 corrects the slight tendency to "chatter" which remains even when using transformer coupling. R_{12} limits the current flowing through the control coil of the Sunvic relay.

The main chassis, the choke L_2, the Sunvic relay and the pilot light are mounted on a thick wooden board which is fixed to the West wall just above the balance slab (see Plate I).

Performance of the room

When the room was first tested, it was found that it would run for long periods at 24.0°C ± 0.1°C without any readjustment of the temperature control. However, if the setting of the three-heat switch was changed, the temperature altered slightly (e.g. changing the setting from medium to high increased the temperature by about 0.1°C.). In practice the switch is set at medium all summer and nearly winter, so this effect is not important.

It has since been found that a fall of 6°C in the external temperature causes the room temperature to rise by about 0.1°C. As there is no part of the controlling resistance in the air stream from the wall fan, this is probably due to slight changes in wall temperature: the effect could therefore be eliminated by mounting the resistance slightly away from the wall. This has not yet been done, as readjustment of the temperature is seldom

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necessary.

The difficulty which was experienced with the old thermoregulator - viz. a change in room temperature when someone entered the room - has been eliminated almost completely. The temperature does not vary by more than 0.05°C when two people enter the room.

It can be seen that the electronic thermoregulator is much more complicated than the paraffin thermoregulator, but does not increase the accuracy of temperature control very much. It is felt that the additional work involved in building it is justified by the simplicity of operation. Once the temperature and bridge adjustments (R_4 and R_5) have been set, they may be left untouched for long periods. If the room is switched off at any time, it can be put into operation again simply by switching on the power to switchboard 4, and allowing the room to run for some hours to reach equilibrium.

D. CONSTRUCTION OF THE THERMOSTAT

The thermostat is similar to that built by Gledhill, but is slightly larger. It consists of an outer vessel filled with water, in which is mounted an inner vessel filled with paraffin. The latter is necessary because for accurate conductance measurements the cell cannot be immersed in water (8).

The outer vessel is of cylindrical shape, 18" in diameter and 2' high. It is made of galvanized iron, and has been painted with bituminous paint to prevent corrosion. As an additional precaution against corrosion it has been filled with distilled water; this also helps to prevent the growth of algae in the water. In it are mounted:

(i) The stirrer. This is a 9" diameter paddle-wheel, which is mounted centrally near the bottom of the thermostat on a long shaft; the top end of this shaft is connected to the axle of a bicycle hub, which is rigidly mounted to an iron framework built into the wall (see Plate II). The stirrer is driven at about 100 r.p.m. by a Garrard gramophone motor, the connection being with a piece of rubber tubing in order to minimize strain on the bearings of the motor. While not designed for such heavy use, the motor has nevertheless proved to be quite satisfactory.

(ii) The heater. This consists of two Cenco 115 volt 250 watt knife blade immersion heaters which are connected in series; they are mounted next to the side opposite the inner vessel. In Gledhill's thermostat there was an asbestos-cement baffle which isolated the heater from the rest of the thermostat, except for a small section near the top and the bottom; a similar baffle was used at first, but was removed for reasons given later.

(iii) The thermoregulator. This is mounted about 3" from the heater on rubber bands, which damp the vibration from the stirrer motor.

(iv) The heat exchange coils. These are made of $\frac{3}{8}$" copper tubing, each coil consisting of two turns about 17" in diameter, flattened on one side to provide space for the baffle and heater. There are three separate coils, but for convenience they have been fastened together by copper rods to form a rigid framework; two of them (A and B) provide purified air for the cell, and the third (C) provides a steady stream of air which stirs the inner vessel.

(v) The potash bulb. This is filled with conductance water, and is joined to coil A; it ensures that the air is saturated with water vapour at 25°C.

(vi) A 5° Beckmann thermometer (made by Siebert and Kuhn). This is used to check the thermostat temperature when taking readings.

The inner vessel is of oval cross section 12" by 6", and is 18" high; it is made of sheet copper. It is mounted close to the wall of the outer vessel on three glass rods 5" long. It contains:

(i) Another heat exchange coil, which is connected to the potash bulb in the outer vessel; air passing through this coil is used for stirring the solution in the cell.

(ii) A tube coil connecting coil B to the cell. Air passing through this coil prevents back-diffusion of carbon dioxide into the cell while taking readings.

(iii) A tube connected to coil C. The air passing through this stirs the paraffin in the inner vessel.

E. CONTROL OF THERMOSTAT TEMPERATURE

The thermoregulator (Fig. V(C))

The type of thermoregulator used by Gledhill has proved to be quite satisfactory, and has been used here.

The thermionic relay (Fig. V(A))

The Gledhill circuit is quite satisfactory for the Struthers-Lunn relay, but had to be modified to operate a Sunvic relay, which requires a much larger control current. The increased current was provided by replacing the 6C5 with a 25L6 (a beam tetrode). In this tube, the potential of the screen grid is kept nearly constant relative to the cathode by the potential divider R_4-R_5.

The alternative arrangement of resistances described by Waddle and Saeman (9) has been used in the grid circuit of V_2. This was necessary because the Sunvic relay, unlike the Struthers-Lunn relay, switches on the load current when the control current flows.

The heater

The heater is capable of dissipating 500 watts, but when the thermostat is operating normally a resistance in series with it limits the current, so that the on and off periods are approximately equal. The resistance consists of a 75 w. 250 v. and a 40 w. 250 v. electric light globe connected in parallel (this combination was

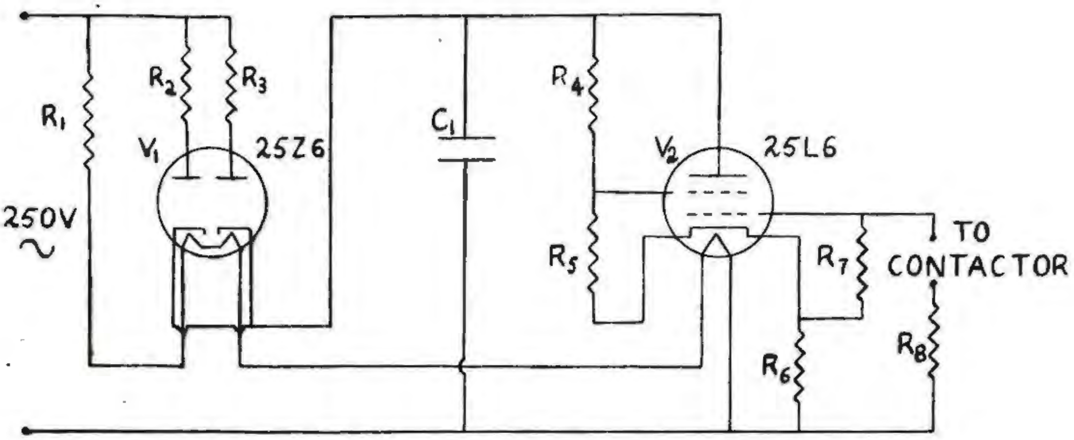


FIG.V(A) CIRCUIT OF THERMIONIC RELAY

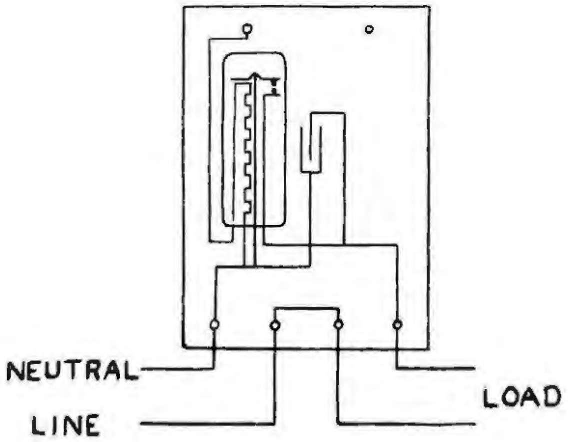


FIG.V(B) SUNVIC RELAY

FIG. V(A). CIRCUIT OF THERMIONIC RELAY

R_1 = 75 watt 230 volt lamp
R_2 = 200 ohms
R_3 = 200 ohms
R_4 = 100 K
R_5 = 15 K
R_6 = Sunvic control element
R_7 = 2 M
R_8 = 200 K

C_1 = 8 μF

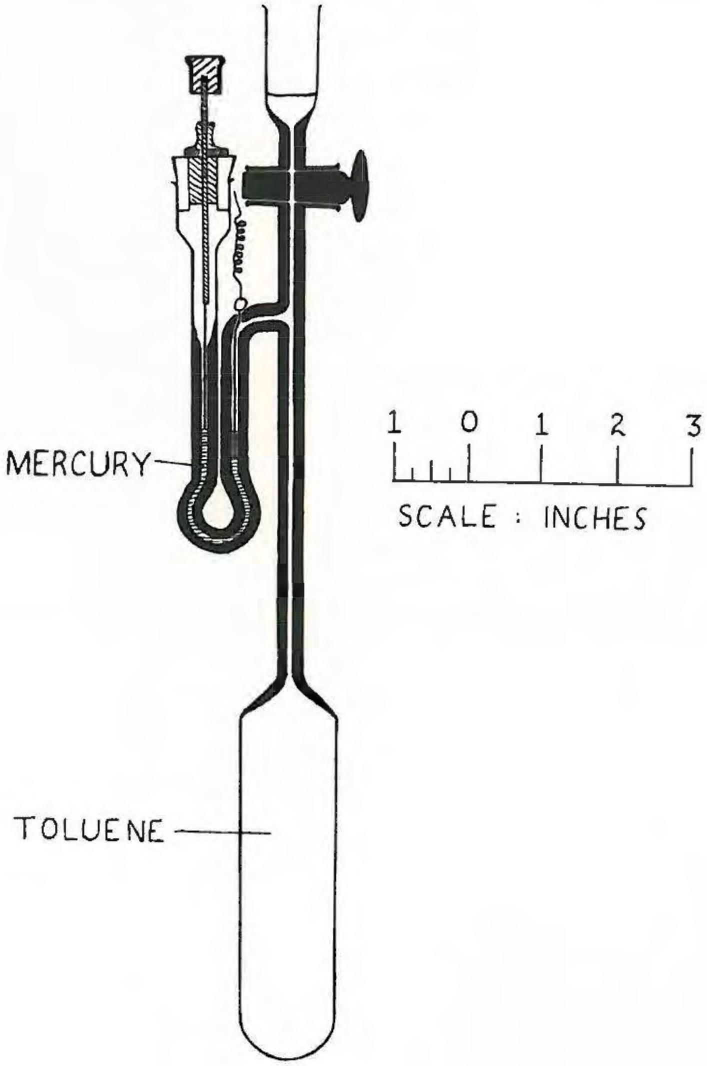


FIG.V(C) THE THERMOREGULATOR

found by trial and error). The globes are mounted outside the c-t room in order to minimize the amount of heat dissipated inside it.

For rapid heating of the thermostat the series resistance may be shorted out by means of a switch.

<u>Performance of the thermostat</u>

When the thermostat was originally tested with the baffle in place, the on-off period was very long, and the temperature in the outer bath varied by about 0.01°C, which was considerably larger than the variation claimed by Gledhill. An examination of the two thermostats showed that the openings allowed for the circulation of the water above and below the baffles were much smaller in the new thermostat than in Gledhill's; this probably accounted for the inferior temperature control.

The baffle was originally installed by Gledhill to prevent currents of hot water from circulating round the main part of the thermostat when the heater was on. Although this is a plausible reason for its use, the effect is not likely to be large in a well-stirred thermostat, and the baffle has a serious drawback: because it impedes the circulation, it tends to build up a supply of hot water round the heater i.e. it effectively increases the heat capacity of the heater. It is well-known that for accurate temperature control it is desirable to use a heater with a small heat capacity, and it was therefore decided to try the effect of removing the baffle.

When the thermostat was tested again, it was found that the on-off period had fallen to about three minutes, and the temperature variation in the outer bath was now only 0.002°C (over a short period. Owing to a leak in the thermoregulator, the temperature rose at the rate of 0.02°C per month: it was reset at fortnightly intervals). In the inner bath it was impossible to detect any variation in temperature on a 1° Beckmann thermometer. As the temperature is read on the thermometer in the outer bath, this means that the maximum error of a temperature reading is 0.001°C, which is satisfactory.

Standardization of temperature

At the time when the experimental work described in Part II was commenced, the position as regards temperature standardization was most unsatisfactory. The most accurate thermometers available were two solid-stem mercury-in-glass thermometers, calibrated in tenths, which had recently been standardized by the South African National Physical Laboratory with an accuracy of ±0.02°C. Fortunately, however, as all measurements (including cell constant determinations) were to be on potassium chloride solutions, it was not essential to set the temperature of the thermostat accurately at 25°C, provided the temperature remained constant between cell constant determinations.

The 5° Beckmann thermometer in the outer vessel was used as the standard thermometer for the experimental work. It was compared as accurately as possible with the two thermometers mentioned above, and on this basis 4.070°C on the Beckmann was taken as 25.000°C.

At a later date a solid-stem mercury-in-glass thermometer calibrated in hundredths became available; this was sent to the S.A.N.P.L. for standardization, and compared with the Beckmann thermometer. It showed that 4.070° on the Beckmann corresponded to 24.97° ± 0.01°C, instead of 25.00°C. However, calculations based on the results of Benson and Gordon (10) show that the temperature coefficients of conductivity of potassium chloride solutions of various concentrations are very nearly the same, so that the error in the measured conductivity will be much less than 0.01%.

Because the volume of the bulb of a liquid-in-glass thermometer changes slowly with time (11), thermometers of this type are not suitable for accurate temperature measurements. For this reason, the possibility that there was a gradual change in thermostat temperature during the conductance measurements must be considered. However, the

F. THE CONDUCTANCE BRIDGE

The theory of alternating current bridges has been worked out in some detail, notable papers being those by Astin (12) and by Ogawa (13). The conductance bridge is a rather specialized form of a.c. bridge; it is unusual because the reactance is not measured nearly as accurately as the resistance. This has the advantage that it simplifies the problem of design, but it also has the disadvantage that it leaves the problem to chemists, who normally do not have much knowledge of electronics and a.c. theory.

The pioneer work on precision conductance bridges was done by Jones and Josephs (14). It is evident from their paper that their approach to the subject was experimental rather than theoretical, and they unjustifiably condemned the use of shielding; nevertheless it seems likely that their bridge was accurate. Since then precision conductance bridges have been described in papers by Shedlovsky (15), who reintroduced the use of electrostatic shielding, by Dike (16), and by Luder (17). The Gledhill bridge was, on the whole, built in accordance with the recommendations of these people, but he showed that their precautions were in some cases unnecessary.

The new bridge described below is modelled on the

The oscillator power supply (Fig. VI (A).)

This is essentially the same as that used by Gledhill, but there are some minor alterations:

(i). The 57 tube was replaced by a 6SJ7 (V_3), which has similar characteristics, but runs off a heater voltage of 6.3v.

(ii). A 1 μF condenser, C_3, from regulated h.t. to earth, and a 0.5 μF condenser, C_4, from the screen grid of V_3 to the control grid, were introduced to eliminate a tendency of the power pack to oscillate.

(iii). The regulated h.t. was connected to the cathode of V_3 through a 2 megohm resistor, R_3, for the following reason: without this resistor, when the value of the unregulated h.t. approached the value of the regulated h.t., the current through V_3 and the neon bulb was very small, and the latter tended to stop conducting. With R_3 in place, the current which flows through the neon bulb from the h.t. is sufficient to maintain the discharge; the regulation is thus improved at low values of the line voltage.

The oscillator is designed to run off 250 v.; by adjusting the variable resistance, R_7, the regulated voltage can be set to this value.

The oscillator (Fig. VII)

When the oscillator was built, it was assumed that the measured resistances would be corrected for polarization by plotting R v. $f^{-\frac{1}{2}}$ (where R = resistance of cell, and f = oscillator frequency), and extrapolating to $f^{-\frac{1}{2}} = 0$. Experience with the other bridge had shown that for satisfactory extrapolation at least five frequencies were desirable; and, as telephones were to be used as an alternative form of detector, the lower and upper frequency limits were fixed at 500 and 2000 c.p.s. Under these conditions, the frequencies which are evenly spaced on an $f^{-\frac{1}{2}}$ scale are:- 500, 653, 889, 1280, 2000.

As it is easier to adjust the oscillator frequencies to harmonics of the line voltage (i.e. of 50 c.p.s.), the frequencies decided upon were:- 500, 650, 900, 1300 and 2000. However, owing to changes in the components of the frequency-determining network, it is no longer possible to adjust the highest frequency to 2000 c.p.s., and it has been adjusted to 1800 c.p.s. The other frequencies are unaltered.

The oscillator is basically of the standard "resistance-capacity phase-shift" type (18) shown in Fig. VI (B). This type of oscillator is capable of giving a very pure wave-form of fairly stable frequency if carefully designed; to do this, the feedback must be adjusted so that it is

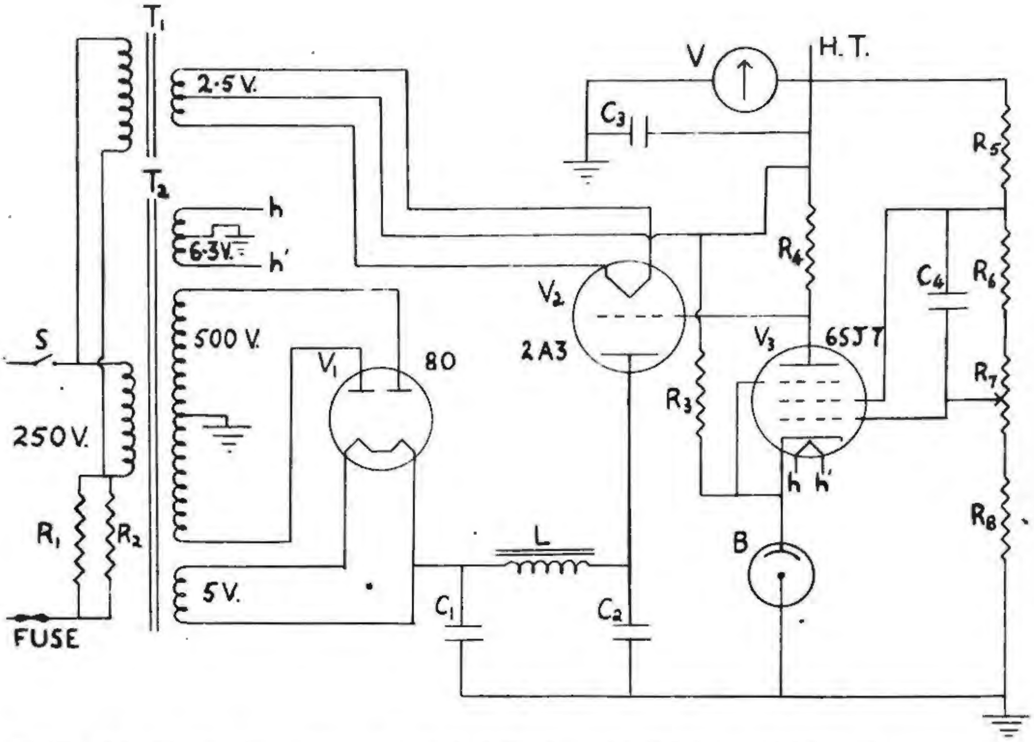


FIG.VI(A) CIRCUIT OF REGULATED POWER SUPPLY

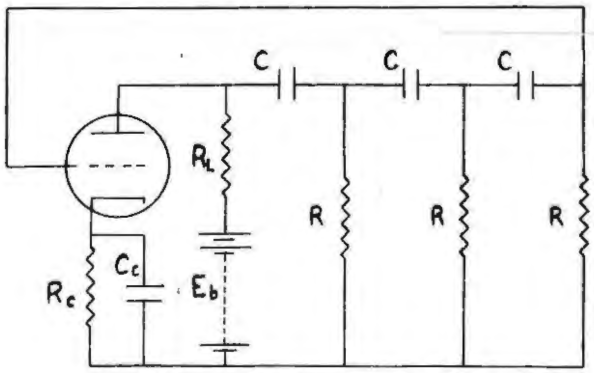


FIG.VI(B) SIMPLIFIED CIRCUIT OF PHASE SHIFT OSCILLATOR

FIG. VI(A). CIRCUIT OF REGULATED POWER SUPPLY

R_1 = 250 ohms
R_2 = 250 ohms
R_3 = 2 M
R_4 = 500 K
R_5 = 20 K
R_6 = 10 K
R_7 = 10 K
R_8 = 5 K
V = voltmeter, 0-300 v.

C_1 = 8 µF
C_2 = 8 µF
C_3 = 1 µF
C_4 = 0.5 µF
L_1 = 30 henries
T_1 = mains transformer
T_2 = 2.5 volt transformer
S = mains switch
B = resistorless neon bulb

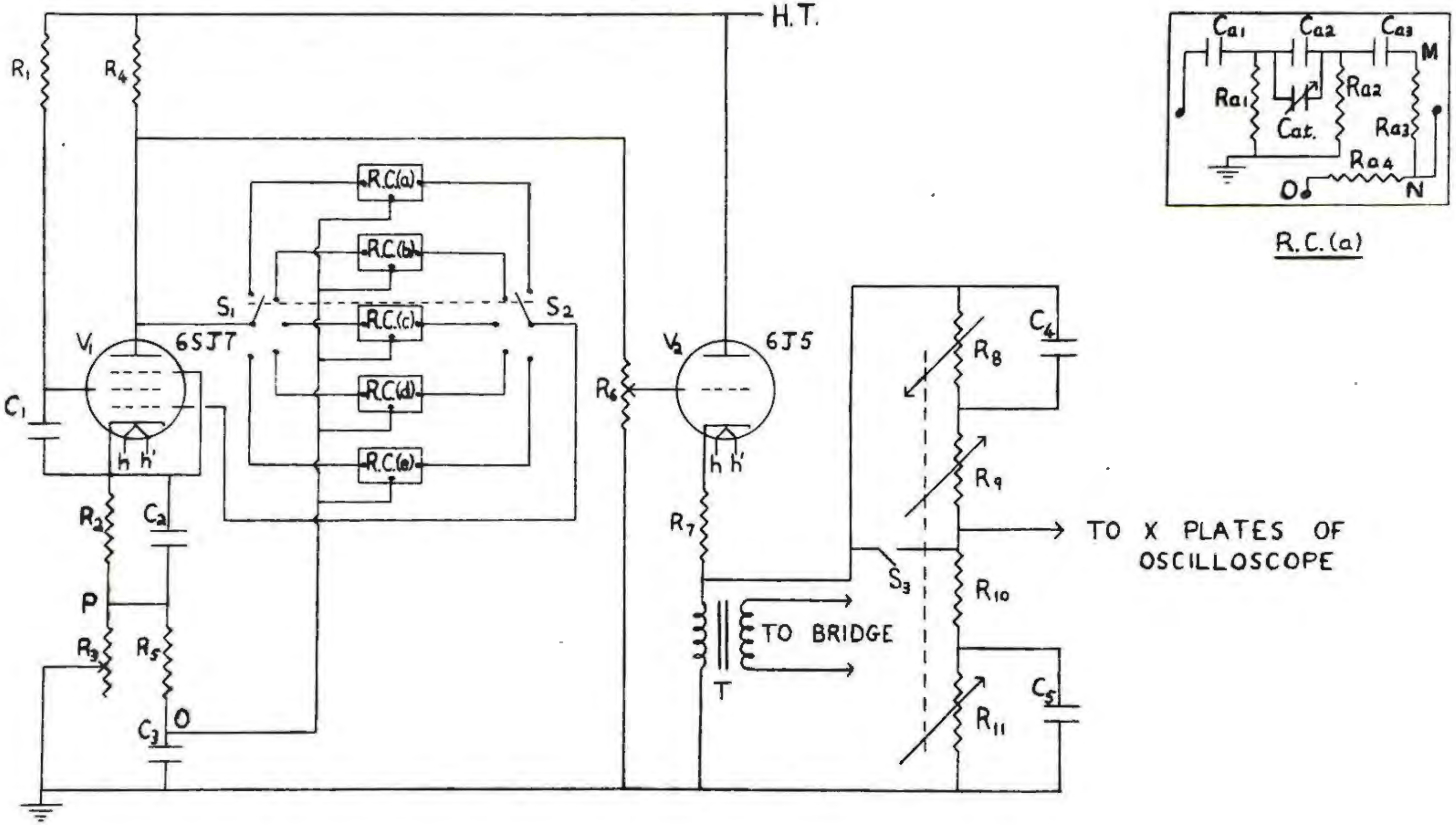


FIG. VII CIRCUIT OF OSCILLATOR

FIG. VII. CIRCUIT OF OSCILLATOR

R_1 = 250 K
R_2 = 200 ohms
R_3 = 1 K
R_4 = 60 K
R_5 = 25 K
R_6 = 250 K
R_7 = 500 ohms
R_8 = 250 K
R_9 = 250 K
R_{10} = 2.5 K
R_{11} = 250 K

C_1 = 0.1 μF
C_2 = 8 μF
C_3 = 0.5 μF
C_4 = 0.01 μF
C_5 = 0.01 μF
T = bridge transformer
(General Radio 578-B)

The CR networks

(a) 500 c.p.s.

R_{a1} = 210 K
R_{a2} = 210 K
R_{a3} = 70 K
R_{a4} = 140 K

C_{a1} = 550 pF
C_{a2} = 550 pF
C_{a3} = 550 pF
C_{at} = 100 pF max.

(b) 650 c.p.s.

R_{b1} = 175 K
R_{b2} = 175 K
R_{b3} = 28 K
R_{b4} = 108 K

C_{b1} = 500 pF
C_{b2} = 450 pF
C_{b3} = 500 pF
C_{bt} = 100 pF max.

(c) 900 c.p.s.

$R_{c1} = 135$ K $C_{c1} = 410$ pF

$R_{c2} = 135$ K $C_{c2} = 420$ pF

$R_{c3} = 12$ K $C_{c3} = 420$ pF

$R_{c4} = 97$ K $C_{ct} = 100$ pF max.

(d) 1300 c.p.s.

$R_{d1} = 145$ K $C_{d1} = 250$ pF

$R_{d2} = 145$ K $C_{d2} = 250$ pF

$R_{d3} = 0$ $C_{d3} = 300$ pF

$R_{d4} = 110$ K $C_{dt} = 100$ pF max.

(e) 2000 c.p.s.

$R_{e1} = 160$ K $C_{e1} = 250$ pF

$R_{e2} = 100$ K $C_{e2} = 160$ pF

$R_{e3} = 0$ $C_{e3} = 200$ pF

$R_{e4} = 205$ K $C_{et} = 100$ pF max.

just sufficient to maintain stable oscillation. In the present case, this has been done by means of:-

(i) a variable adjustment which operates at all frequencies.

(ii) five fixed adjustments - one for each frequency - built into the frequency-determining CR networks.

Adjustment (i) is the variable resistance R_3 in the cathode circuit of V_1. The principle of operation is briefly as follows:-

Condenser C_3 is of negligible impedance to a.c., but of almost infinite impedance to d.c. Because of this, O will be at the same potential as P with respect to d.c., but at earth potential with respect to a.c. Hence variation of R_3 will not affect the grid bias (which is determined by the value of R_2), but will vary the a.c. potential of the grid with respect to the cathode. As the tube current is not much affected by this adjustment, the degeneration is proportional to the value of R_3.

An adjustment of type (ii) consists of a potential divider in the third "leg" of the CR network (see Fig VII). The frequency-determining resistance is the total value between points M and O, but the voltage fed back is proportional to the ratio NO : MO. It was found that with the CR networks connected in the conventional manner, the amount of degeneration required to give a pure

wave-form varied greatly with frequency, being least at the highest frequency. For this reason the potential divider was omitted at the highest frequency, and the adjustment of the ratio NO : MO for the other four frequencies was carried out as follows:-
The oscillator was set to 2000 c.p.s., and R_3 adjusted until it was just oscillating. The setting of R_3 was then left untouched, and the ratio NO : MO adjusted for stable oscillation by trial and error for each of the other four frequencies. In this way the oscillator was made to give a pure wave-form at all five frequencies for one setting of R_3.

Owing to the change in the component values mentioned before, it is now necessary to reset R_3 when changing from 1800 c.p.s. to one of the lower frequencies. However, by noting the best setting of R_3 in each case, the adjustment can be made rapidly.

The frequency of oscillation is given by

$$f = \frac{1}{2\pi CR\sqrt{6 + 4R_1/R}} \qquad \text{(A)}$$

where $R_1 = \frac{R_L . R_P}{R_L + R_P}$, and R_P = a.c. resistance of the tube. Other symbols as shown in Fig. VI (B).

Owing to stray capacities in the wiring, and the large tolerances of the components used, it was found that formula (A) was not reliable. The final selection of the components for the CR networks was therefore done by trial and error. In order to adjust the frequencies accurately, a 100 pF trimmer condenser C_t has been included in each CR network. The adjustment is done with the aid of the oscilloscope by the method of Lissajous figures.

The 6J5 (V_2) is a buffer tube; it prevents changes in loading from affecting the frequency and stability of oscillation. Owing to the large amplitude of oscillation - about 60 volts - it is not a disadvantage if the 6J5 has an effective amplification factor which is less than one. Accordingly this tube has been connected as a cathode follower, which is notable for combining a very low output impedance with a very high input impedance. Even with this arrangement, an undistorted output of 8 volts is easily obtainable. As 2 volts applied to the bridge gives sufficient sensitivity, and in fact cannot be used when measuring small resistances without causing heating effects, the bridge transformer T (General Radio type 578-B) has been connected so that the voltage is stepped down. This has the following advantage:-
The impedance, Z_{in}, between the primary terminals of a transformer is given by

$$Z_{in} = n^2 . Z_{out}$$

where n = ratio of primary to secondary turns

and Z_{out} = impedance connected across secondary winding. With the 578-B transformer, when the voltage is stepped down, $n = 4$: hence $Z_{in} = 16Z_{out}$.
When the voltage is stepped up, $n = \frac{1}{4}$, and $Z_{in} = \frac{1}{16} Z_{out}$. The former is obviously better, as a small impedance can be measured without overloading the oscillator. It has been shown that even when measuring a resistance of 100 ohms it is possible to apply a pure wave-form of 1 volt r.m.s. to the bridge.

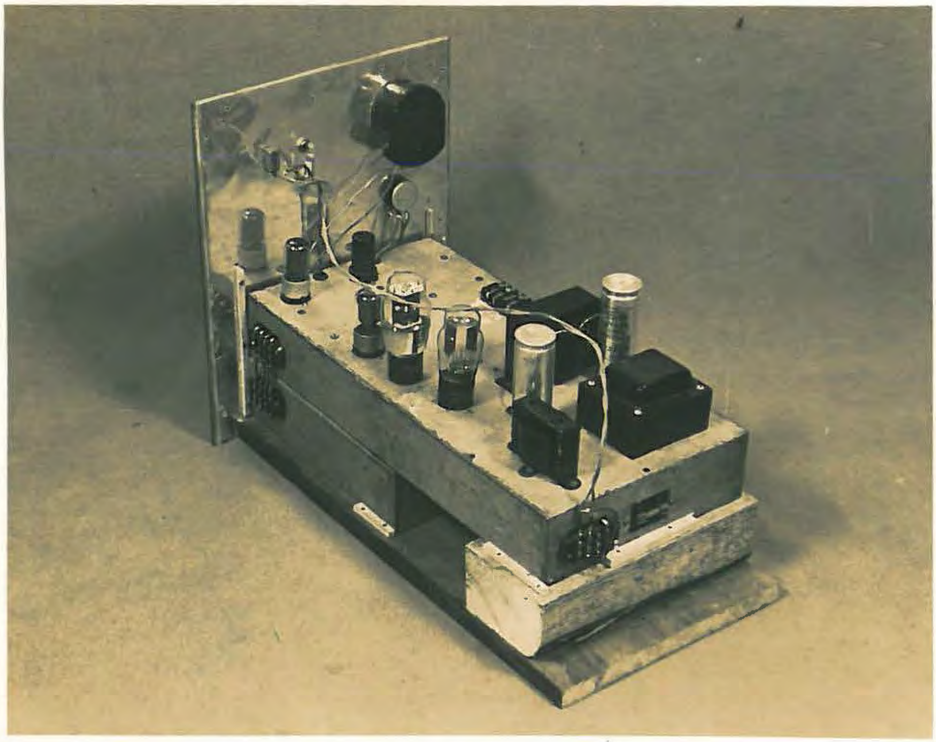
When the oscillator output was connected to the transformer through a condenser, distortion of the wave-form resulted. The cause of this is not known, but the effect has been overcome by connecting the transformer primary in series with the cathode resistor of V_2.

The phasing device

This consists of the network R_8, R_9, R_{10}, R_{11}, C_4 and C_5. The output voltage can be adjusted to be anything from -81° to $+85^{\circ}$ out of phase with the input voltage by means of the ganged potentiometer R_8-R_9-R_{11}. The use of the device will be explained later.

Mechanical construction of the oscillator

The main part of the oscillator and its power supply have been built into one large chassis (see Plate IV). The power supply is shielded from the rest of the circuit with 20 gauge galvanized iron, as was done by Gledhill;



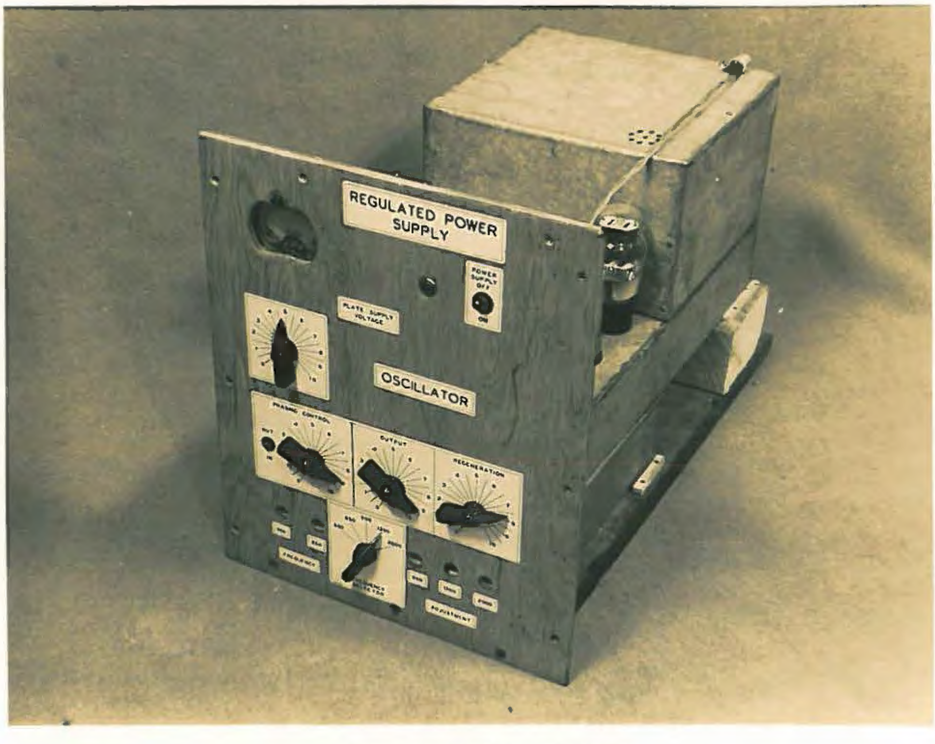

REGULATED POWER SUPPLY
POWER SUPPLY OFF
ON
PLATE SUPPLY VOLTAGE
OSCILLATOR
PHASING CONTROL
OUT
IN
OUTPUT
REGENERATION
FREQUENCY
FREQUENCY SELECTOR
ADJUSTMENT

PLATE IV

but as the oscillator does not contain any inductance, this precaution is probably unnecessary.

Because of the large number of components in the CR networks, and the necessity for making the trimmers easily accessible, all these components were built into a separate chassis mounted beneath the main chassis. This type of construction has the additional advantage that the heat from the tubes does not reach the components of the CR networks: thermal drift of frequency is thus avoided.

All controls are brought out to the front panel. They are:- the power switch S, with pilot light; the plate supply voltage control R_7, with voltmeter; the degeneration control R_3; the output control R_6; the frequency-selector switch S_1S_2, and the five frequency adjustments, C_{at}, C_{bt}, C_{ct}, C_{dt}, C_{et}; the phasing control R_8-R_9-R_{11}; and the switch S_3.
(Note: S_3 was installed so that the oscillator output can be connected directly to the X-axis amplifier of the oscilloscope, which can then be used to check roughly the voltage applied to the bridge.)

The amplifier (Fig. VIII)

In the Gledhill bridge the two chief factors limiting the sensitivity are stray a.c. pick-up from the unshielded parts of the bridge, and the impure wave-form of the oscillator. As the effect of both these factors would be diminished by increasing the selectivity of the amplifier, some time was spent in attempting to do this.

A paper by Scott (19) describes a very selective amplifier employing degenerative tuning in the following way: the output from a three-stage amplifier is fed back to the input through a combination of resistances and condensers known as the "twin-T network". This network has zero output at one frequency, so that the gain of the amplifier will be unaltered at this frequency; but at all other frequencies it will be considerably reduced by the negative feedback.

An attempt was made to build an amplifier of this type, but it was unsuccessful for two reasons:-

(i) Owing to phase changes in the amplifier at high frequencies, the use of the twin-T network caused it to oscillate. To eliminate this effect the amplifier design would have had to be considerably improved.

(ii) If the values of the components used in the twin-T network alter slightly, the amplifier will either tend to oscillate, or else will have its gain considerably reduced. As the only resistors available were of the carbon type, this was a serious objection.

It is probable that these difficulties could have been overcome, but at this stage the amplifier described below was built. Although the selectivity is undoubtedly much less than that of Scott's, it was found to be sufficient.

The form of tuning which was finally used is the conventional parallel resonant circuit, which is placed in the plate load of the tube. It has two advantages:

(i) There is only a small voltage drop in the plate load: consequently a fairly small h.t. voltage (180 v.) may be used.

(ii) Owing to the large a.c. resistance of the parallel resonant circuit (in this case more than 1 megohm), a high gain per stage is obtainable.

As the exact values of the inductances used were unknown, the value of the capacitance for each resonant circuit was determined experimentally.

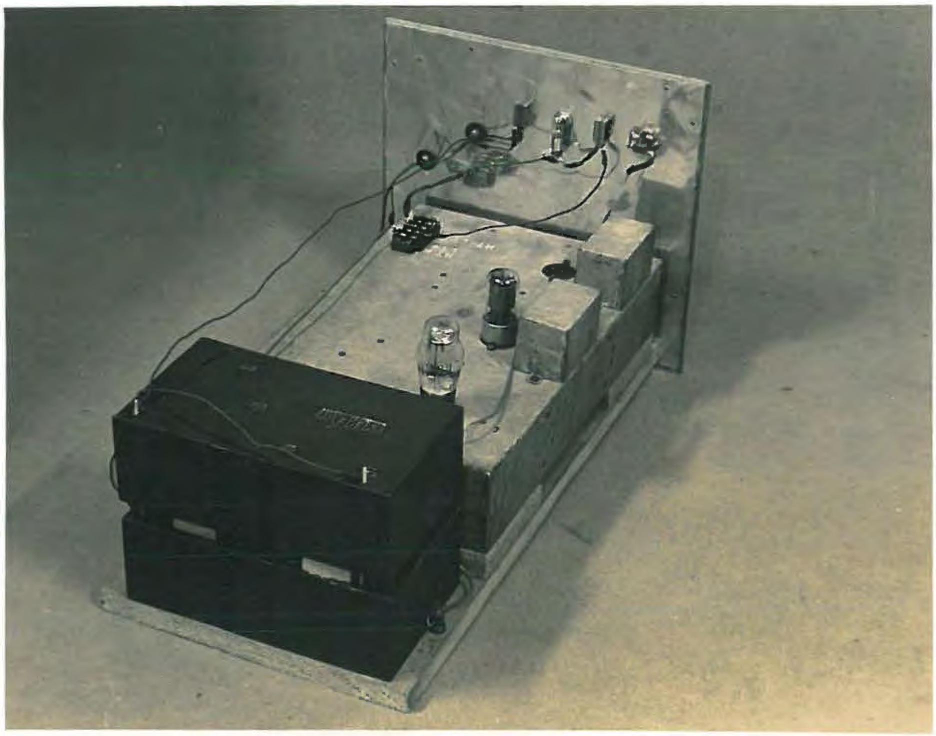
There is heavy decoupling in each plate circuit to prevent feedback from the output to the input stage through the h.t. line. The amplifier is run off batteries, to avoid a.c. pick-up, and to avoid interaction between the oscillator and amplifier through the mains. The A-battery is a 6 volt lead accumulator, which is kept charged by means of a trickle charger. The B-batteries are 45 volt batteries of the type normally used in portable radios. A switch in the h.t. supply line enables the operator to switch off the h.t. in the intervals between readings, thus prolonging the life of the B-batteries; the current through the tube heaters is left on during these intervals, so that the amplifier can be brought into operation immediately.

Two terminals marked "H.T.+" and "H.T.-" have been installed on the front panel, so that the condition of the B-batteries can be checked without having to remove the amplifier from the bridge. A phone jack is connected to the output of the amplifier, as it was intended to use the telephone as a detector if the oscilloscope went out of order. For d.c. operation of the bridge, a terminal marked "GALV" is included; this is connected to the input of the amplifier.

Mechanical construction of the amplifier

The amplifier is built into a chassis 10 x 16 x 3 ins., (see Plate V), which is divided into three compartments by transverse strips of metal. Each compartment contains one stage of the amplifier, which is thus shielded from the other two stages. Further shielding has been effected by enclosing the two chokes L_1 and L_2 completely in boxes made of galvanized iron, and by making all connections between stages with shielded wire.

Jones, Mysels and Juda (20) found that the first tube of a high-gain amplifier often acts as a microphone, and the electric signals produced are amplified by later



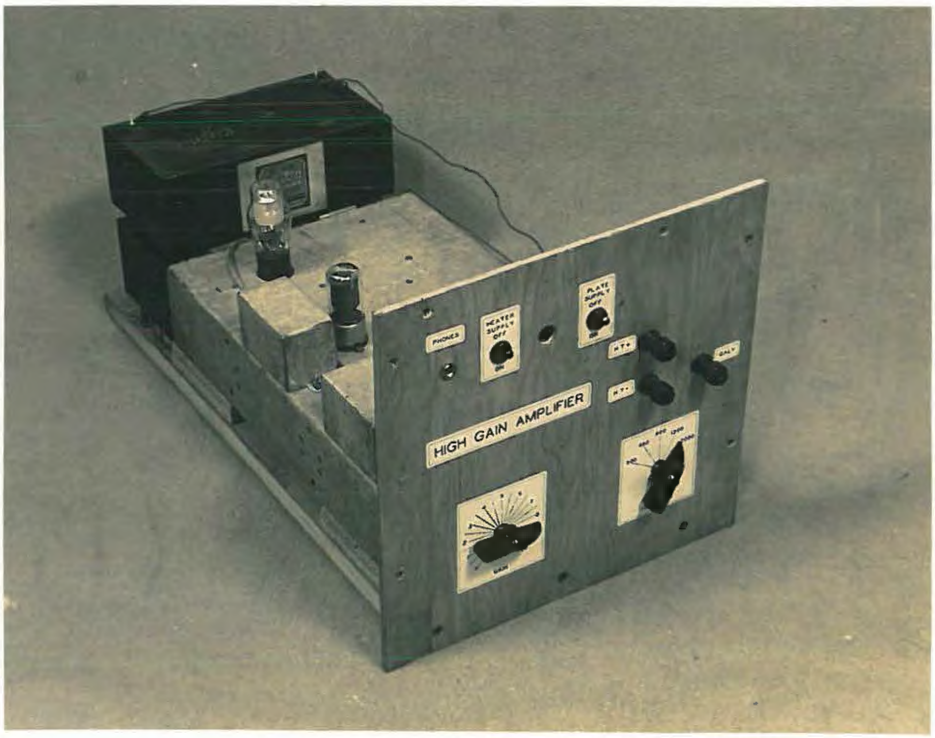

PHONES
HEATER SUPPLY OFF ON
PLATE SUPPLY OFF ON
H.T.+
H.T.-
GALV
HIGH GAIN AMPLIFIER
GAIN

PLATE V

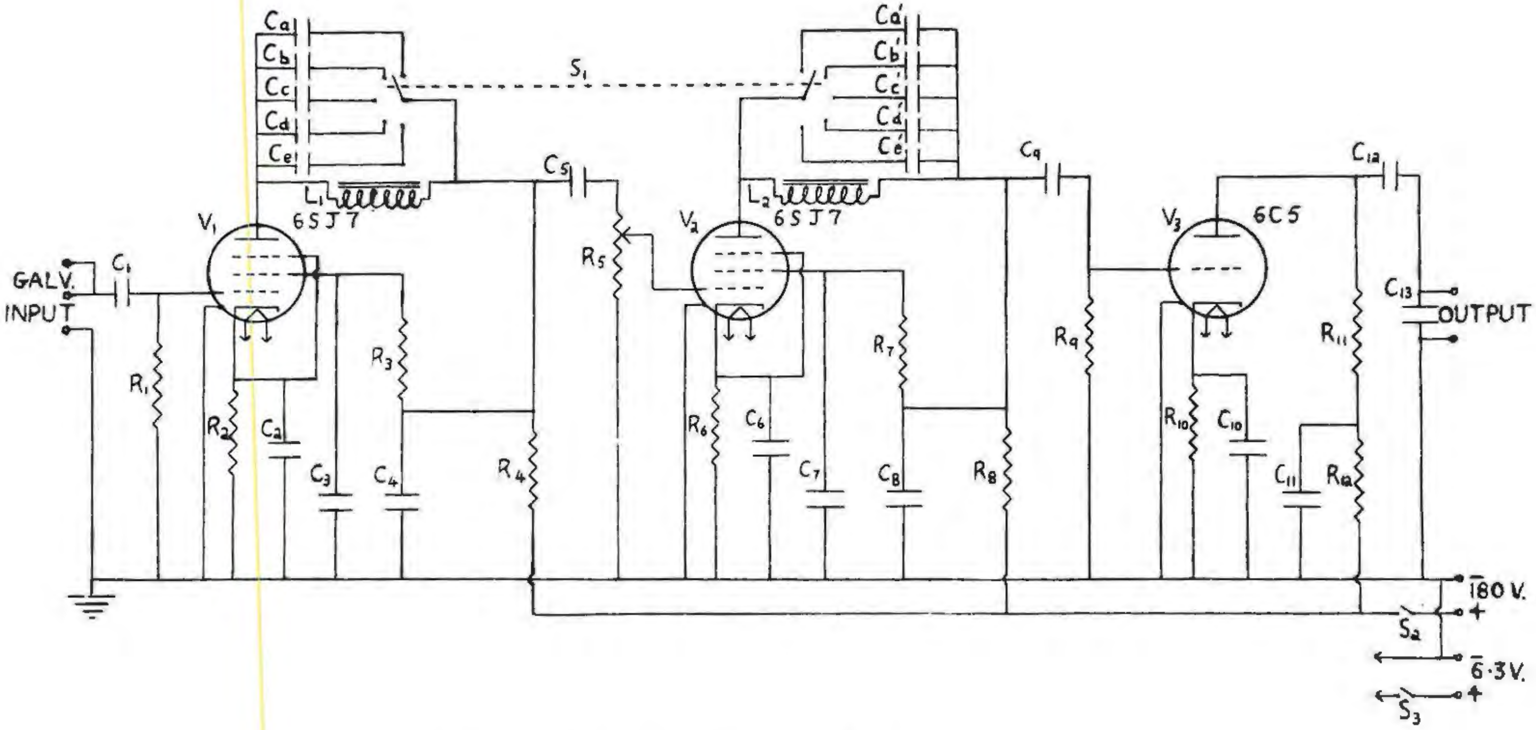


FIG VIII CIRCUIT OF AMPLIFIER

FIG. VIII. CIRCUIT OF AMPLIFIER

R_1 = 1 M
R_2 = 600 ohms
R_3 = 500 K
R_4 = 5 K
R_5 = 1 M
R_6 = 600 ohms
R_7 = 500 K
R_8 = 5 K
R_9 = 500 K
R_{10} = 3.5 K
R_{11} = 100 K
R_{12} = 5 K
L_1 = 10 henries
L_2 = 10 henries
C_a = 8650 pF
C_b = 5450 pF
C_c = 2700 pF
C_d = 1600 pF
C_e = 600 pF

C_1 = 0.05 μF
C_2 = 8 μF
C_3 = 0.06 μF
C_4 = 8 μF
C_5 = 0.006 μF
C_6 = 8 μF
C_7 = 0.6 μF
C_8 = 8 μF
C_9 = 0.006 μF
C_{10} = 8 μF
C_{11} = 8 μF
C_{12} = 0.1 μF
C_{13} = 0.003 μF
$C_{a'}$ = 8400 pF
$C_{b'}$ = 5300 pF
$C_{c'}$ = 2600 pF
$C_{d'}$ = 1450 pF
$C_{e'}$ = 550 pF

◆

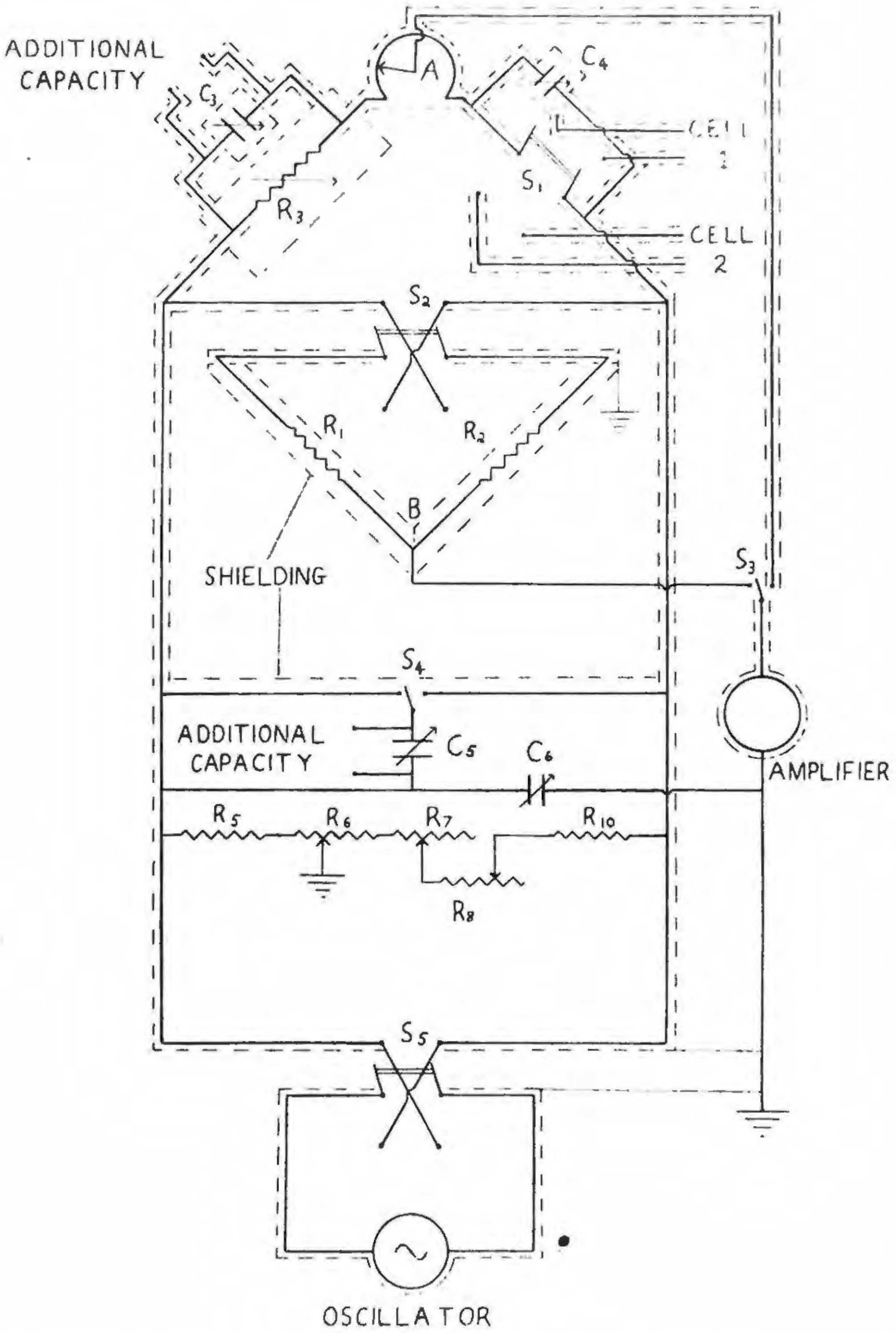


FIG.IX CIRCUIT OF CONDUCTANCE BRIDGE

FIG. IX. CIRCUIT OF CONDUCTANCE BRIDGE

R_1 = 10,000 ohms
R_2 = 10,000 ohms
R_3 =111,111 ohms max.
R_5 = 10,000 ohms
R_6 = 1,000 ohms
R_7 = 50 ohms max.
R_8 = 5 ohms max.
R_{10}= 10,000 ohms

C_3 = 340 pF max.
C_4 = 105 pF max.
C_5 = 320 pF max.
C_6 = 100 pF max.

---

stages. They state that mounting the amplifier on air-foam rubber reduces the sensitivity to noises considerably; this recommendation has been carried out.

As in the case of the oscillator unit, all controls are brought out to the front panel. They are: the heater supply switch S_3, with pilot light; the plate supply switch S_2; the gain control R_5; the frequency-selector switch S_1; the phone jack; and the terminals "GALV", "H.T.+" and "H.T.-".

(Note: As the gain of the amplifier originally built was found to be unnecessarily high, the second stage shown in Fig. VIII has been removed, leaving a two-stage amplifier.)

The amplifier-bridge connection

Two methods are commonly used for connecting the bridge output to the amplifier:-

(i) The direct method, in which the amplifier is connected between A and B (Fig. IX) to balance the main bridge, and between earth and A to balance the Wagner earth. As it is desirable to earth the amplifier, a coupling transformer must be used.

(ii) Separate terminal balancing, which is the method shown in Fig. IX.

Separate terminal balancing was used by Gledhill, but since it has the disadvantage that the Wagner earth has to be balanced as accurately as the main bridge, the possibility of using method (i) was considered. However, it was decided to adhere to the method of separate terminal balancing, as it is more accurate: a coupling transformer of the type normally used will decrease the sensitivity of the bridge as the resistance being measured. (Luder (21) mentions this effect.) This defect could be overcome by using a transformer with a high impedance primary, but this is undesirable, as it would increase the likelihood of a.c. pick-up, and of interaction between oscillator and amplifier (see Astin (12)).

A third possibility is the use of a doubly-shielded ungrounded amplifier, as recommended by Dye and Jones (22). It was felt that the additional trouble involved in the construction of such an amplifier was not warranted by the small additional convenience obtained.

Interaction between oscillator and amplifier

In a conductance bridge electrostatic shielding is a comparatively simple matter, but electromagnetic shielding is not. It was, of course, lack of electromagnetic shielding that caused the interaction between oscillator and amplifier mentioned by Jones and Josephs (23). They (and other early workers in this field) overcame the difficulty by mounting the oscillator more than 10 feet from the main bridge assembly; but, as a conductance bridge contains no inductance, once the transformer coupling the amplifier to the bridge has been removed, the absence of electromagnetic shielding is unimportant, and it is no longer necessary to take this precaution. Luder apparently did not realize this, and followed the conventional practice. Gledhill showed that mounting the oscillator and amplifier close together did not introduce any error, but did not give any theoretical reason for this.

In the present case, as separate terminal balancing is used, it has also been possible to mount the amplifier and oscillator in the same framework. To confirm the absence of interaction, the input to the amplifier was disconnected at S_3; it was then impossible to detect any a.c. in the amplifier output, even with maximum output from the oscillator.

(Note: If there is interaction between oscillator and amplifier, which produces a small voltage dV which is p^o out of phase with the bridge input voltage (i.e. dV, p) zero output can still be obtained in the amplifier by adjusting the bridge until its output is dV, 180 + p. If separate terminal balancing is used, then points A and B will be at the same potential (i.e. provided the interaction remains constant when changing from "ratio arms" to "measuring arms"), and the bridge will be accurately balanced: current can, of course, flow to earth from both A and B, but as these points are only at potential dV with respect to earth, the error will be negligible. With a coupling transformer, however, $V_B - V_A = dV$, so that the bridge will not be accurately balanced.)

The detector

The detector used in the bridge is a cathode ray oscilloscope (Dumont type 208-B).

The types of null detector used in balancing a.c. impedance bridges may be classified under three main headings:-

(i) The telephone.

(ii) Galvanometers (either a.c. or, with rectification, d.c.).

(iii) Electronic visual indicators.

The most common of these is undoubtedly type (i), the telephone, due to its low cost and relatively high sensitivity. It requires a quiet environment for precise balance, and is not phase discriminating i.e. resistive and reactive components cannot be balanced separately.

Type (ii), the galvanometer, is a visual indicating device, and therefore the need for quiet is eliminated. The a.c. galvanometer, by proper adjustment of the phase of the magnet current, can be made phase selective; however, it has to be readjusted each time a change of phase is wanted, and it it not possible to observe the degree of unbalance of both phases simultaneously. Another objection to its use is that at maximum sensitivity a transient disturbance will overload the galvanometer, so that a considerable time must elapse before it can be used again.

Type (iii) can be either a "magic eye" (similar to that used in radios), or a cathode ray oscilloscope. Lamson (24) has pointed out that the oscilloscope is superior to any other form of detector for the following reasons:-

(a) The observations are visual, and may be carried on in the presence of external noise.

(b) Extreme unbalance merely causes a harmless movement of the image off the screen, instead of a deafening noise in the telephone, or a surge of current in the galvanometer which renders it inoperative for a considerable time.

(c) The chief advantage of the oscilloscope lies in its discrimination between the resistive and reactive components of the voltage. This is accomplished in the following way: if the oscillator output is fed to the X-plates in correct phase, and the bridge output voltage (suitably amplified) is fed to the Y-plates, then at balance there will be a horizontal line on the screen.

A slight unbalance in the resistive component will tilt this line through a positive or negative angle, depending on the sign of the error in balance; an error in the reactive balance will convert the line into an ellipse (see Plate VI). It is obvious that precise balance of the resistive component can be obtained without the trouble of equally precise balance of the reactive component. Jones, Mysels and Juda (25) have applied this method of detection to a precision conductance bridge with very satisfactory results.

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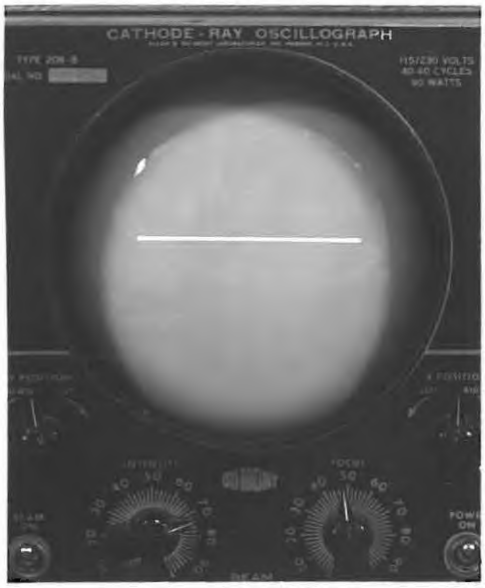
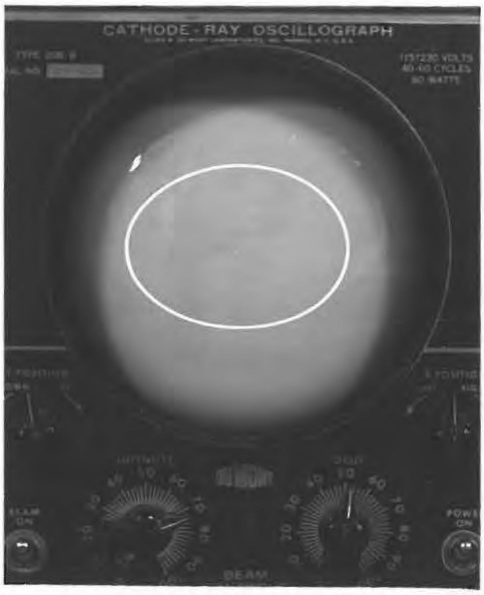
Knife switches

As it was impossible to obtain knife switches with a distance of 1½ inches between contacts (the distance recommended by Gledhill), it was necessary to modify those which were available. The arms and contacts were removed from their original bases, and the arms lengthened by riveting onto them suitable lengths of $^1/_{16}$ inch copper strip, the join being soldered to ensure good electrical contact. The arms and contacts were then riveted to ebonite bases at suitable distances apart. In this way three double-pole double-throw and two single-pole double-throw switches were made. The handles of the former were constructed wholly of ebonite to minimize the leak between the two arms. The rivets holding the contacts of the switches extend to the bottom

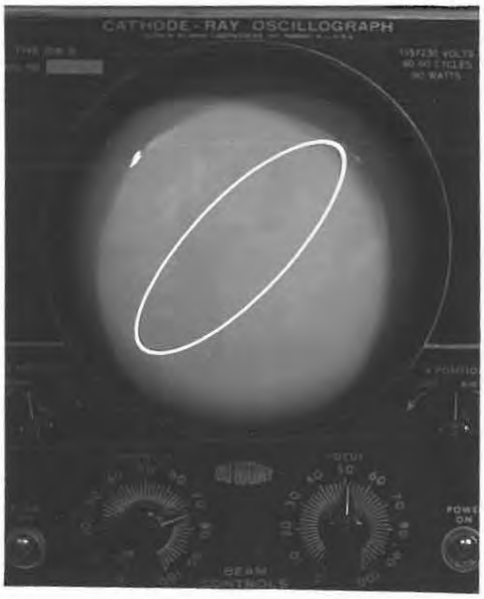


BALANCE



REACTIVE UNBALANCE

RESISTIVE UNBALANCE



COMBINED UNBALANCE

PLATE VI

of the ebonite bases: therefore, to prevent any leak across the surface of the panel to which they are fixed, the switches were mounted on ebonite washers.

It was also necessary to make eleven single-pole double-throw knife switches for the 10,000 ohm decade. Instead of making these singly, the arms and contacts were riveted to one large board of ebonite.

While calibrating the bridge it was found that the switches described above had a variable contact resistance. After some preliminary experiments, it was found that this could be remedied by riveting a silver contact into the arm of the switch. The cell selector switch, the ratio arm switch, and the first switch in the 10,000 ohm decade have been modified in this way: in the case of the other switches, a very low contact resistance is not essential.

Design of the front panel

In planning the general lay-out of controls on the front panel, as far as possible the knife switches were placed near the outer edge of the bridge, and the fine capacity adjustments near the centre. With this arrangement, the hands of the observer are far away from exposed terminals when making final adjustments, thus minimizing hand-capacity effects.

The Wagner earth (See Plate VII)

The Wagner earth panel consists of: a double-pole double-throw switch (S_5) for reversing the supply voltage; an a.c.-d.c. switch which determines the bridge current; three resistance adjustments - coarse, medium and fine; coarse and fine capacity adjustments (C_5 and C_6); two terminals (marked "additional capacity") for connecting additional capacities in parallel with C_5; and a single-pole double-throw switch (S_4) for connecting C_5 either to the cell-arm side or the measuring-arm side of the bridge.

The coarse resistance adjustment is a 1000 ohm potentiometer, R_6, whose centre-tap is the earthed point of the Wagner earth; the medium adjustment is a 50 ohm variable resistance, R_7; and the fine adjustment is a 5 ohm variable resistance, R_8.

The coarse capacity adjustment is a 320 pF variable air condenser, C_5; the fine adjustment C_6 is of the same type, with maximum capacity 100 pF. Both condensers are fitted with slow-motion drive, the reduction ratio in the case of C_6 being quite large.

Individual shielding of the Wagner earth components is unnecessary, it being the purpose of the Wagner earth to balance out stray capacities.

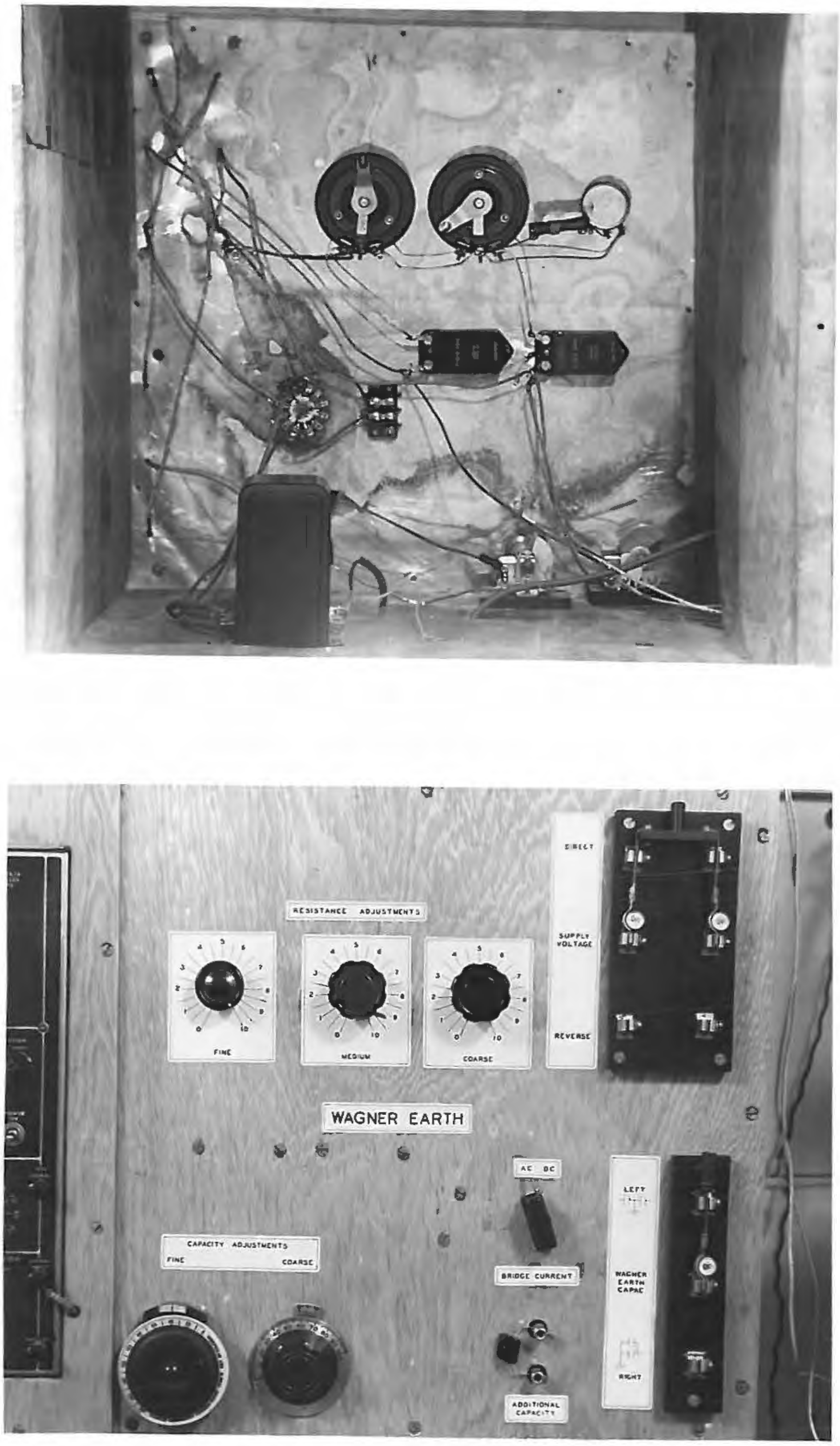

RESISTANCE ADJUSTMENTS
FINE
MEDIUM
COARSE
DIRECT
SUPPLY VOLTAGE
REVERSE
WAGNER EARTH
AC DC
CAPACITY ADJUSTMENTS
FINE
COARSE
BRIDGE CURRENT
ADDITIONAL CAPACITY
LEFT
WAGNER EARTH CAPAC
RIGHT

PLATE VII

The measuring arm

The 0.1, 1, 10, 100, 1000 and 10,000 ohm resistance decade units are General Radio types 510-A, -B, -C, -D, -E and -F respectively. The shields supplied with the units have been removed, and they are mounted at a minimum distance of 2½ inches from the shielding, in accordance with the conditions laid down by Shedlovsky (26); he says: "If the upper frequency range does not exceed 4000 cycles, direct test showed that a separation of 2.5 inches between the coils of the resistance box (or cell) and the shield introduces a negligible error." In view of the fact that the 1000 and 10,000 ohm decades of Shedlovsky's bridge were mounted in an oil-filled thermostat, a separation of 2.5 inches may well be unnecessarily large.

Except for the 10,000 ohm decade, which is connected in a special way, all the decades are mounted on a subsidiary piece of plywood situated 3 inches behind the front panel; in this position the resistances are more than 3 inches from the shielding attached to the front panel. In order to bring the control knobs to the front panel, the spindles of the decades were extended with special ebonite rods supplied by the General Radio Company. The 1000 ohm decade was modified in the way described by Gledhill (loc. cit.), as the switch in his bridge has been very satisfactory. The diameter of the modified unit is 18 cm.

The 10,000 ohm decade was completely dismantled and rebuilt according to the design of Luder (27). The advantage of this design is that all resistances not in use are completely disconnected, thus eliminating "dead-end" effects. As described previously, eleven knife switches have mounted 4 cm. apart on a large ebonite board, which is mounted 5 inches behind the front panel. The method of wiring the resistances in this decade can be seen in Plate IX (the two leads at the right edge of the picture are connected as shown in Plate VIII). There is a hinged section of the front panel in front of the board to provide access to the knife switches. All switches except one are normally down; if the first switch is up, the 10,000 ohm decade is disconnected; if the second switch is up, the first 10,000 ohm resistance is connected; and similarly for the other switches.

<u>The slidewire</u> between the cell and measuring arms was made specially for the bridge, as nothing suitable was available commercially. It consists of a circular disc of ebonite 4 inches in diameter, with a piece of thick resistance wire about 10 inches long (resistance slightly greater than 0.05 ohms) fixed in a groove in the circumference. The sliding contact is a suitably shaped strip of beryllium copper, which is rigidly connected by a

strip of ebonite to a spindle passing through the centre of the disc. The other end of the spindle is fitted with a 2 inch bar knob, which indicates the slidewire setting on a circular scale on the front panel. Readings on the scale are easily reproducible to within 0.001 ohm.

The method of connecting the slidewire is that used by Dike (16). It has the advantage that the resistance of the sliding contact is in series with the amplifier input. Dike states that the method of connecting C_3 and C_4 introduces a negligible error, and this has been confirmed by calculation. It should be noted that when the point of contact is moved, the resistance is increased on one side of the bridge and decreased on the other. for this reason the range of the slidewire is twice its total resistance.

(Note: The slidewire had not yet been installed at the time the photograph (Plate VIII) was taken. It is mounted in the blank space beneath the tens decade.)

The parallel condensers in the measuring arm (C_3) and the cell arm (C_4) of the bridge are ordinary variable air condensers of maximum capacities 340 pF and 105 pF respectively. There is a pair of terminals for the connection of fixed condensers in parallel if the capacity of C_3 is not sufficient; the "additional" condensers are of the

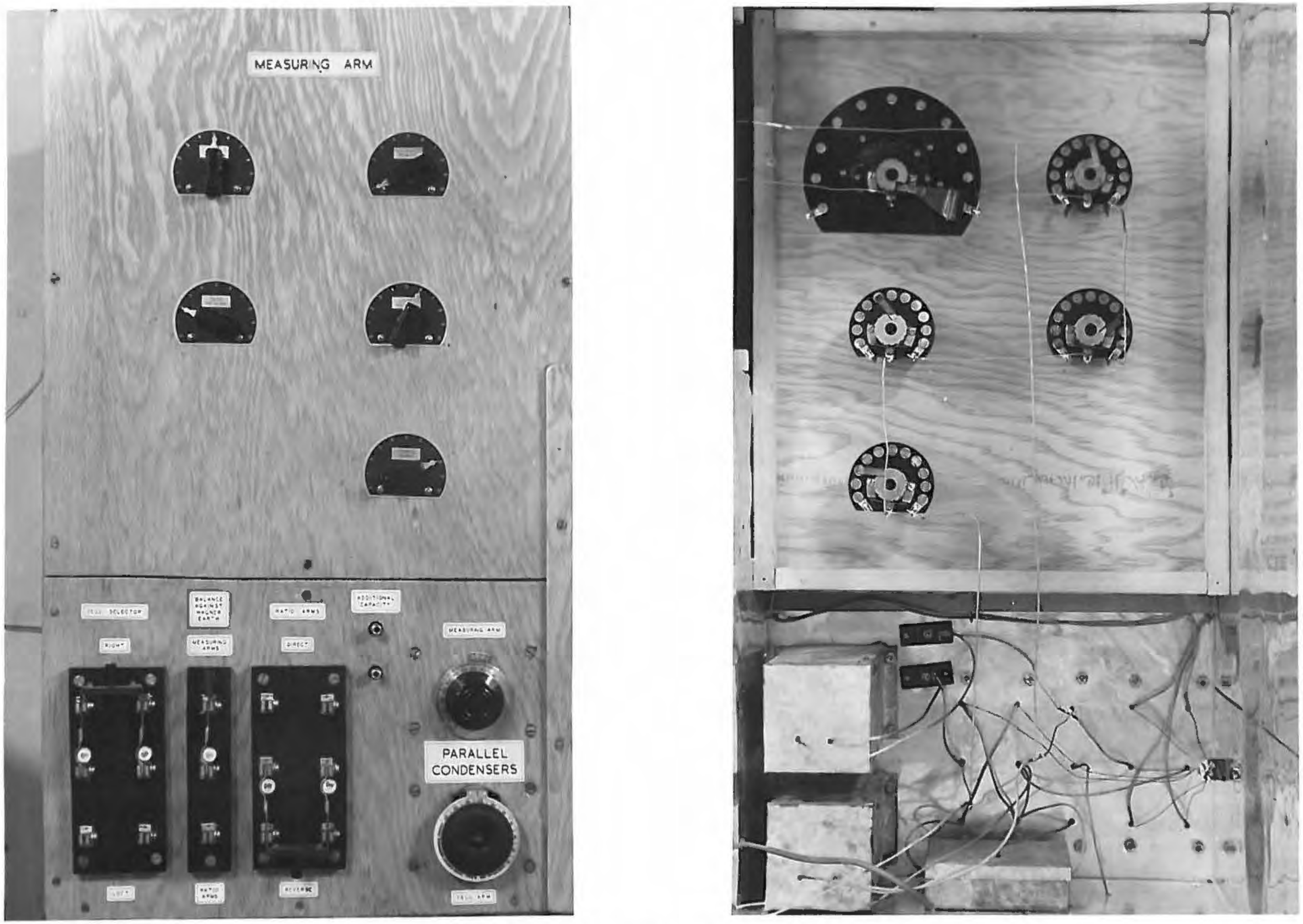

MEASURING ARM
CELL SELECTOR
RIGHT
LEFT
BALANCE AGAINST WAGNER EARTH
MEASURING ARMS
RATIO ARMS
RATIO ARMS
DIRECT
REVERSE
ADDITIONAL CAPACITY
MEASURING ARM
PARALLEL CONDENSERS
CELL ARM

PLATE VIII

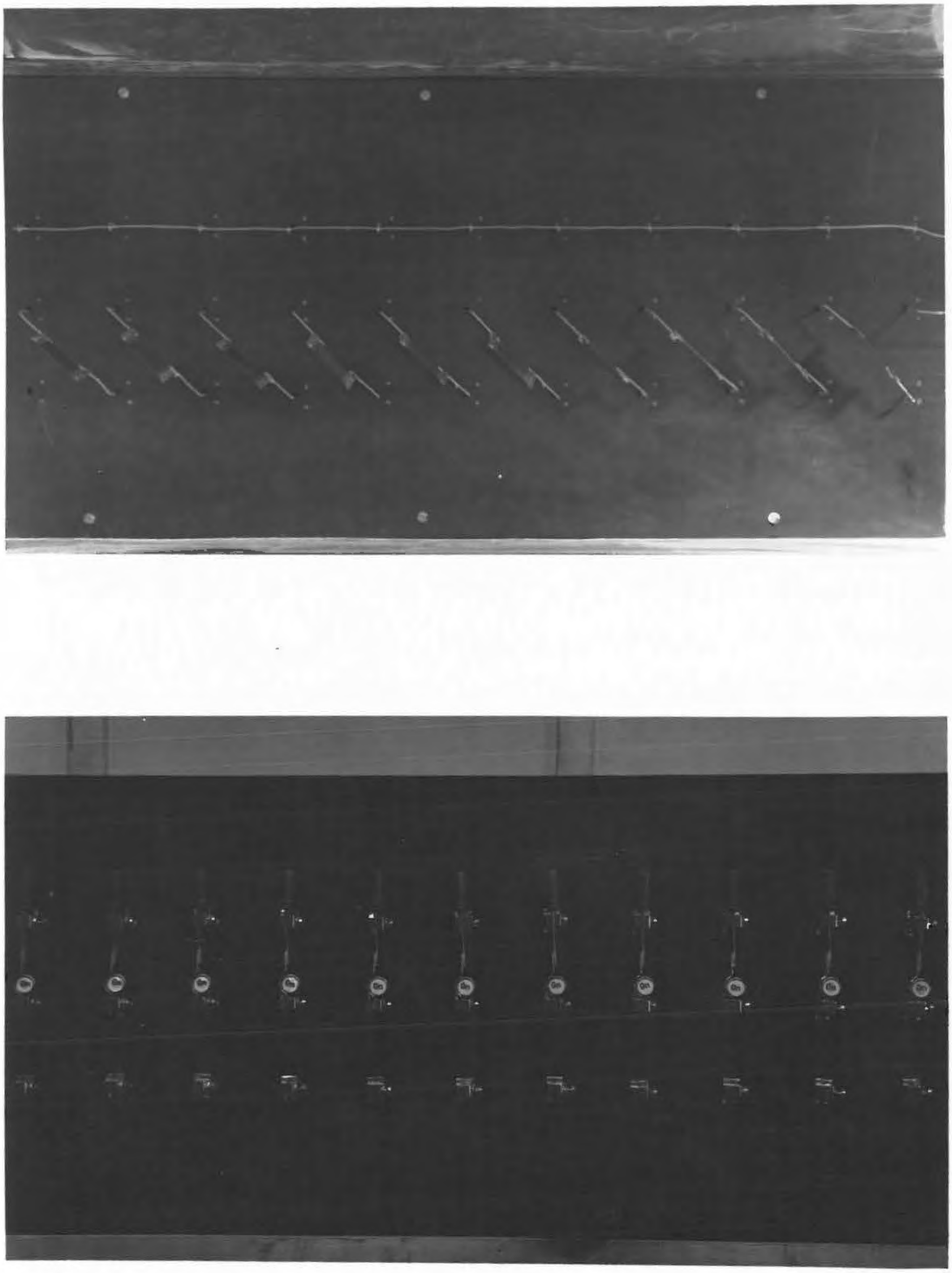


PLATE IX

mica type. (Where the additional capacity required was large, and the resistance being measured small, a General Radio type 219-M decade condenser box was used as well; but it was later found that in some cases this could introduce errors, and its use is therefore not recommended.)

C_3 and C_4 are shielded separately in cases made of galvanized iron. Each condenser is screwed onto an ebonite base fixed to the shielding case, which is bolted to the front panel (see Plate VIII). As the movable plates of the condensers are connected electrically to the driving shafts, it is desirable that these be insulated from the slow-motion drives, in order to avoid hand-capacity effects. This has been done by extending the shafts with $1\frac{1}{2}$ inch lengths of ebonite rod.

The calibration of the condensers was carried out as follows: C_4 was disconnected and the cell leads connected to a General Radio type 500-J resistor (10,000 ohms, non-inductive). A standard variable air condenser (from the Physics Department) was placed in parallel with the resistor, and the bridge balanced for various settings of C_3. After C_3 had been calibrated in this way, the various condensers which were to be used as additional capacities were placed in parallel with C_3(set to a specified value); the bridge was then balanced by adjusting the standard condenser. This gave the values of the additional capacities. C_4 was then reconnected, the standard condenser removed, and the bridge balanced for various settings of C_4. In this way C_4 was calibrated in terms of C_3.

The ratio arms

It is clear that the ratio arms may be closely shielded, as the reversing switch S_2 compensates for slight inequalities in the impedance. The resistance of each arm is 10,000 ohms, the resistors being of the General Radio type 500-J. They are mounted in a close-fitting galvanized iron box, which is divided into two halves shielded from each other. To keep the connecting leads short, the ratio arms were mounted directly behind S_2.

The other two switches mounted on the front panel are the cell selector switch S_1, and the switch S_3, which connects the amplifier input either to "ratio arms" or to "measuring arm".

Insulation tests

The maximum resistance to be measured directly on the bridge is 10^5 ohms; the accuracy aimed at was 0.001%. Accordingly the insulation of components in the cell and measuring arms should be greater than 10^{10} ohms.

The most convenient method for testing the insulation was the condenser leak method. Gledhill says that this method has the serious disadvantage of being time-consuming, quoting a standard discharge time of 60,000 seconds. The necessity for such a long time was due to the fact that he used a standard condenser of capacity 2 microfarads. As the time t required for discharge is proportional to CR (where C = capacity of condenser, and R = resistance being measured), it is clear that t may be reduced by using a smaller capacity. Using a capacity of 0.338 microfarads, it was possible to cut down the discharge time to 3,600 seconds, which is not excessive. In spite of the smaller capacity used, it was found that a potential of only 0.75 volts was sufficient to give full scale deflection of the galvanometer.

Insulation tests were carried out on the following:

(i) Two of the knife switches which had been rebuilt, chosen at random.

(ii) The two parallel condensers, C_3 and C_4.

(iii) The additional condensers used in parallel with C_3.

In all cases the insulation had a resistance greater than 10^{10} ohms.

It was unnecessary to test the insulation between the two "additional capacity" terminals, or that of the shielded wires, as leaks in these instances would be to earth, and would therefore be balanced out by the Wagner earth.

Conditions for balance of the bridge

The actual equivalent circuit of a conductance cell is not known, but it is generally assumed that it can be represented approximately by a resistance (the true resistance of the cell) in series with a capacity (C_s); the circuit of the conductance bridge is then as shown in Fig. X(A).

The general condition for balance is

$$\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4}$$

where Z = a.c. impedance of each arm.

Now $Z_1 = Z_2$ (approximately).

Therefore for balance $Z_3 = Z_4$.

By imagining a capacity C_4 in parallel with Z_3' and Z_4' (Fig. X(B).), it can easily be seen that $Z_3 = Z_4$ when $Z_3' = Z_4'$.

Let $C_3 - C_4 = C$

Then, using the well-known formula for impedances in parallel

$$Z_3' = \frac{R_3 \cdot \frac{-j}{pC}}{R_3 - \frac{j}{pC}} = \frac{R_3}{1 + p^2C^2R_3^2} - \frac{jpCR_3^2}{1 + p^2C^2R_3^2}$$

where $p = 2\pi$ times the a.c. frequency

and j is the symbol of rotation of a vector through 90°; $j^2 = -1$.

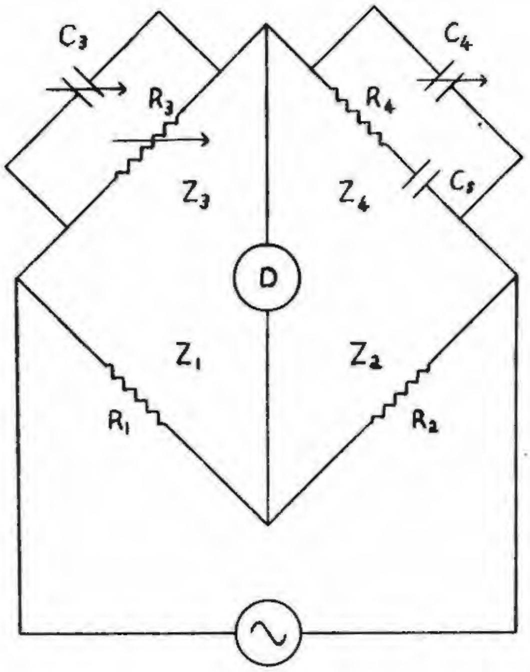


FIG.X(A) SIMPLIFIED BRIDGE CIRCUIT

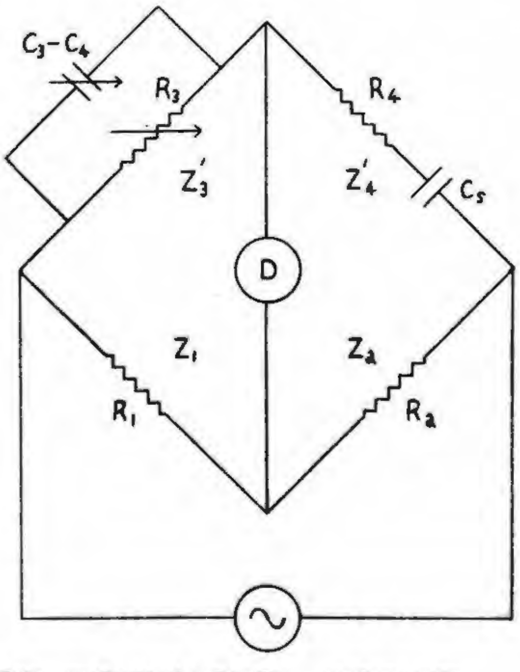


FIG.X(B) EQUIVALENT CIRCUIT

Also $Z_4' = R_4 - \frac{j}{pC_s}$

Equating resistances: $R_4 = \frac{R_3}{1 + p^2C^2R_3^2}$

$$= R_3(1 - p^2C^2R_3^2)\text{.......}(A)$$

since $p^2C^2R_3^2$ is much less than 1.

Equating reactances: $\frac{1}{pC_s} = \frac{pCR_3^2}{1 + p^2C^2R_3^2}$

$$C_s = C(1 + \frac{1}{p^2C^2R_3^2})\text{.......}(B)$$

The conditions for balance are therefore given by (A) and (B).

In practice Z_1 is not exactly equal to Z_2. Readings are therefore taken with the ratio arms direct and reversed, and the arithmetic mean is taken as the true resistance.

Performance of the bridge

On the whole the bridge has proved to be satisfactory, and the oscilloscope is definitely a more convenient detector than the telephone. With the present arrangement, however, it suffers from two disadvantages:

(a) It is necessary to reset the phasing control each time the frequency of the oscillator is changed.

(b) If it is left on for long periods, the oscillscope (which dissipates 90 watts) warms up the 10,000 ohm decade, causing a small change in resistance. This limits the use of the bridge, but was no drawback in the work described in Part II, as readings were only taken occasionally.

During the first part of the work on potassium chloride, it was found that the bridge was not accurate when measuring resistances of the order of 100 ohms e.g. using a setting of 90 ohms on a General Radio decade box as standard, the bridge reading increased by 0.005 ohms on changing the frequency from 500 to 1800 c.p.s. As the effect was small, no attempt was made at the time to eliminate it, but a correction was applied to all readings. Later, however, when it became necessary to measure resistances over a wide frequency range (see Part II (D).); it was found that the bridge was very insensitive at high frequencies, and that this was mainly due to the long shielded leads connecting the cell selector switch to the cell; when these were replaced by short lengths of coaxial cable, the sensitivity improved, and the bridge reading was found to be independent of frequency (i.e. using a General Radio 10 ohm decade without shielding as a standard).

Later the accuracy of the bridge when measuring larger resistances was also tested, using carbon resistors as standards. (These resistors have negligible reactance at audio frequencies, but the resistance is not constant. However, by taking readings at constant intervals, it

was possible to correct for the drift in resistance.)
It was found that at settings of 760, 3500, 5000 and 9800 ohms the reading was independent of frequency, but at 13,000 ohms $R_{500} - R_{1800} = 0.4$ ohms, and at 36,000 ohms $R_{500} - R_{1800} = 0.9$ ohms. It is unlikely that the effect is due to the 10,000 ohm resistors, and it appears that Luder's type of 10,000 ohm decade is not entirely free from error. It is possible that capacitive shunts between the terminals of the knife switches would account for the effect, but this theory has not been tested.

Suggested improvements in the bridge

In the light of the experience gained in building and using the bridge, the author would like to suggest the following improvements:

Amplifier It has been found that although the telephone is available as a stand-by, it is never used; if the oscilloscope does go out of order, it is preferable to repair it before continuing with research work, as it is much more convenient to use. Under these circumstances there is no need to use a triode for the output valve, and consequently the amplifier could easily be redesigned to draw very much less current from the B-batteries.

Rough experiments have shown that it should be possible to dispense with the A-battery, which could be replaced by a trickle charger with a smoothing circuit electronic switching circuit to give a double-beam oscilloscope. This would be used in conjunction with a second bridge output amplifier; switch S_3 (Fig. IX) would be eliminated, and the operator would be able to to balance the measuring arm and Wagner earth simultaneously. In cases where the conductance is changing rapidly this arrangement would greatly increase the accuracy of the bridge.

Bridge circuit: In view of the superior insulation and lower capacity per foot of coaxial cable compared to ordinary shielded wire, it is recommended that the entire bridge circuit be rewired with coaxial cable.

Calibration of the bridge (Oct. 1949 and Aug. 1951)

The calibration of the bridge was done in two stages:

(i) The resistances in a separate decade resistance box were intercompared. (This box will hereafter be called Q.)

(ii) The bridge resistances were compared with the resistances in Q.

This rather involved procedure was adopted because there did not appear to be a simple method of intercomparing the bridge resistances directly.

Q was originally an ordinary d.c. resistance box with five decade units (1, 10, 100, 1000 and 10,000 ohms). To facilitate the intercomparison, the switching mechanism was removed, and mercury cups were made in all the studs which had been the switch contacts. All the wiring connecting the decade units was removed.

Before commencing the calibration, one stud on the 10,000 ohm decade was disconnected from the rest of the decade. The resistance between this stud and the others was then measured by the condenser leak method, and found to be greater than 10^{10} ohms.

The resistances of Q were compared by the well-known Carey Foster bridge method (see e.g. (29)). Although this has been superseded by more accurate methods (Mueller (30) says: "The use of (the Carey Foster bridge method) is rapidly acquiring the status of one of the lost arts, and references to papers describing it will be omitted here, lest someone be tempted to revive it."), it was sufficiently accurate for this purpose. Each 10,000 ohm resistance was compared with the sum of the 1000's, each 1000 with the sum of the 100's, and so forth. In the case of the 1 ohm decade, the first resistance (1_1) was taken as standard, 1_2 and 1_3 as ratio arms, and 1_4 to 1_{10} in turn as unknown; this gave 1_4 to 1_{10} in terms of 1_1. The ratio arms were then changed to 1_4 and 1_5, and 1_1, 1_2, and 1_3 were compared with 1_6.

The comparison of bridge resistances with the resistances of Q was carried out by connecting the galvanometer between A and B (Fig. IX). This procedure was adopted to make the setting of the Wagner earth less critical; actually it was found that the setting did not affect the balance point at all, even when comparing resistances of 100,000 ohms.

The following voltages were used in the measurements on Q:

Resistance	Voltage across resistor
1 ohm	0.08 volts
10 ohms	0.25 volts
100 ohms	0.75 volts
1,000 ohms	1.5 volts
10,000 ohms	3.0 volts

In the case of the 1, 100 and 1000 ohm resistances it was shown experimentally that these voltages gave errors less than 0.001% due to heating effects.

When calibrating the conductance bridge, the voltage across individual resistors was always less then the values given above.

When doing the second calibration, the 1 ohm resistances were assumed to have the same correction as before. All the 10 ohm resistances in Q were intercompared, but only the settings 5 to 10 in the 10 ohm decade of the bridge were checked.

Measurement of small resistances

The small resistances were calibrated by comparing the voltage drops across a standard 0.1 ohm resistor and the unknown resistance, using a Tinsley vernier potentiometer. This method was used for the 0.1 ohm decade, the conductance bridge slidewire, the Carey Foster bridge slidewire, and the bridge lead resistances.

For the second calibration the resistances of the Carey Foster bridge slidewire and the bridge leads (which had been changed) were measured. All other resistances were assumed to be the same as before.

Standard resistance

As there was no standard resistance available for the first calibration, it was decided to use the sum of the 100 ohm bridge resistances as an arbitrary standard. However, shortly afterwards a 10 ohm oil-immersed resistor of the Reichsanstalt pattern was borrowed from the Physics Department and sent to the S.A.N.P.L. for standardization. It was compared directly with the sum of the 1 ohm resistances, and with the first resistance in the 10 ohm decade of the bridge, before and after standardization. This is not a good method of comparing the standards, as the variation in switch contact resistance may be as much as 0.001 ohm, but it would have been inconvenient just then to set up the Carey Foster bridge again. The comparison showed that the two standiffered by 0.122 %.

In the second calibration, the 10 ohm resistances of Q were compared directly with the 10 ohm standard, and as mercury cups were used, errors due to contact resistance were negligible. On comparing the two values of the 76 resistances which had been calibrated twice, it was found that 69 of these differed by about 0.12 %; the mean of the 69 differences is 0.118%. Considering the uncertainty mentioned previously, this is in very good agreement with the value 0.122 % given above. The mean (0.120%) was taken as the difference between the two standards, and was used to convert the results of the first calibration to the 10 ohm standard. It was found that the maximum change in any individual resistance between calibrations was 0.023%, and the maximum change in correction for any setting of the bridge decades was 0.009%.

PART II

THE CONDUCTIVITIES OF POTASSIUM CHLORIDE SOLUTIONS

A. INTRODUCTION

Although the conductivities of KCl solutions have often been measured during the past twenty-five years (e.g. see (10), (31, 32, 33, 34, 35, 36, 37)), there is a possible source of error that has not been mentioned: the adsorption of KCl on the surface of glass (or quartz). On several occasions changes in conductance have been attributed to adsorption, but in all cases it was assumed that this took place on the platinized electrodes. However, as similar effects were observed by P. X. Faure (38) even when using unplatinized electrodes, it seemed possible that it was a source of error in the measurements mentioned above. Owen and Zeldes (31), Daggett, Baer and Kraus (32), Shedlovsky (33), Grindley and Davies (34), Davies (35) and Krieger and Kilpatrick (36) made up their solutions by adding KCl to conductance water in the cell; Li and Fang (37) and Benson and Gordon (10) rinsed out their cells with KCl solutions of known concentration, which had presumably been prepared in carefully-cleaned containers.

It was therefore decided to measure the conductivities of dilute KCl solutions with special precautions to prevent adsorption errors. Solutions were always made up exactly to a certain concentration in a flask which was never rinsed with water or dried; therefore, even if adsorption on glass does take place, it would reach an equilibrium value in the first solutions, and not affect the concentration of the later ones. In the same way adsorption in the cell would reach an equilibrium value.

B. THE APPARATUS

The following apparatus was used in addition to that described in Part I;

Balances

B I is a Kuhlmann microbalance (beam length 7 cm.). This balance is not in perfect condition, but with light loads will weigh to within 10 micrograms.

B II is an air-damped Oertling balance fitted with a device whereby all weights less than 1 g. can be manipulated with the balance case closed. Maximum load is 100 g., accuracy 0.1 mg. This balance is mounted on the slate slab in the c-t room.

B III is a large Sartorius balance, maximum load 1000 g.

The difference in length of the arms of each balance was determined by the double-weighing method: a suitable correction was applied to all weighings. In the case of B I this correction increased slowly, and was redetermined occasionally.

Weights

W I is a box of Grade A plated-brass Sartorius weights (10 mg. to 100 g.), which was used with B I and B II.

W II is a box of brass weights (10 mg. to 1000 g.) which was used with B III.

W III is the set of riders supplied with B II (10 mg.

to 0.5 g.); these were used for all weighings on B II.

The two 10 g. weights from W I had very nearly the same mass, and the mean was taken as 10.0000 g. All weights less than 10 g. were compared with these on B I (to 10 micrograms); this calibration was repeated several times. Weights from 10 to 100 g. from W I, all weights less than 100 g. from W II, and the weights W III were intercompared on B II. The other weights from W II were compared on B III.

Conductance cells

Two types of Pyrex conductance cell were used:

(i) A cell designed by Gledhill for conductimetric titrations, in which special care was taken to avoid "Parker effect" (39). The original design was modified to give better stirring; the new version is shown in Fig. XI.

When in use, purified air from coil A (p. 26) is passed through tube A to stir the solution in the cell and remove carbon dioxide; while taking readings the stirring is turned off, and air from coil B is passed through tube B to prevent back-diffusion of carbon dioxide. The top of the cell is normally covered with a closely-fitting glass cap (the fit is not close enough to impede the circulation of air).

The cell is supported in the thermostat by the rubber tubing connecting it to the thermostat coils.

(ii) A cell basically the same as the well-known Jones cell, but fitted with a "stirring tube", so that the solution may be swept out by carbon-dioxide-free air (see Fig. XII). It was realized shortly after making it that the modified version was liable to Parker effect, due to capacities between the mercury cups and the filling tubes. However, as removal of carbon dioxide from the cell is very desirable, it was decided to use it in the range in which Parker effect is not appreciable.

The solution in the cell is stirred as follows: Pure air is passed in through tube I, and forms a bubble in the stirring tube S; when this is large enough, it breaks off and drifts along S to O, where it rises to the surface of the liquid. There is thus a steady stream of bubbles along S, stirring the solution and removing the carbon dioxide. As the stirring is turned off while taking readings, O is fitted with a soda-lime guard tube to prevent back-diffusion of carbon dioxide.

The cell is suspended in the thermostat from S. The support is a piece of "Perspex" 11 x 2½ inches, with slots for the filling and lead tubes.

Cell I is of type (i), and was used exclusively for measuring the conductivity of water.

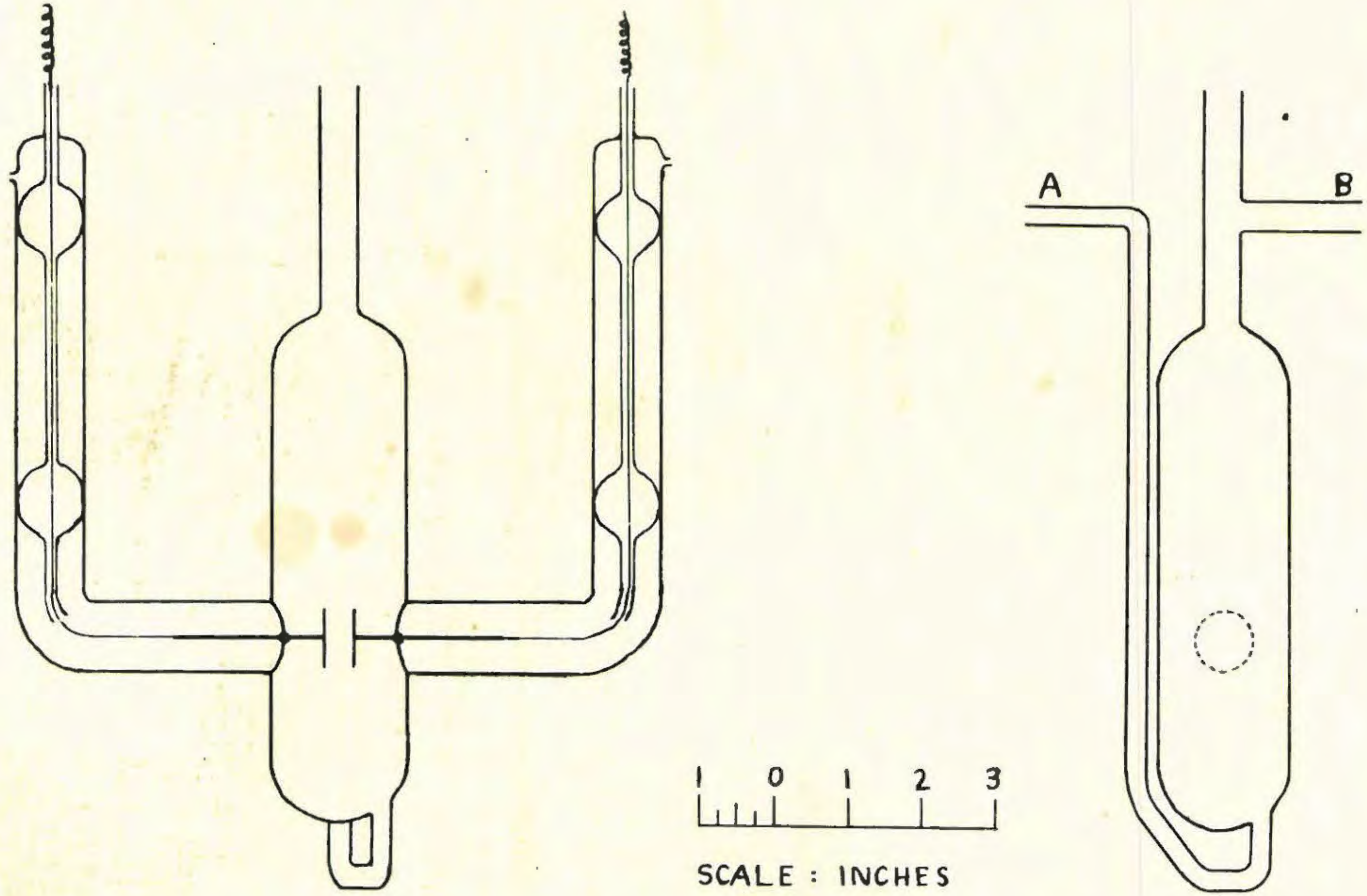


FIG. XI CELL 1

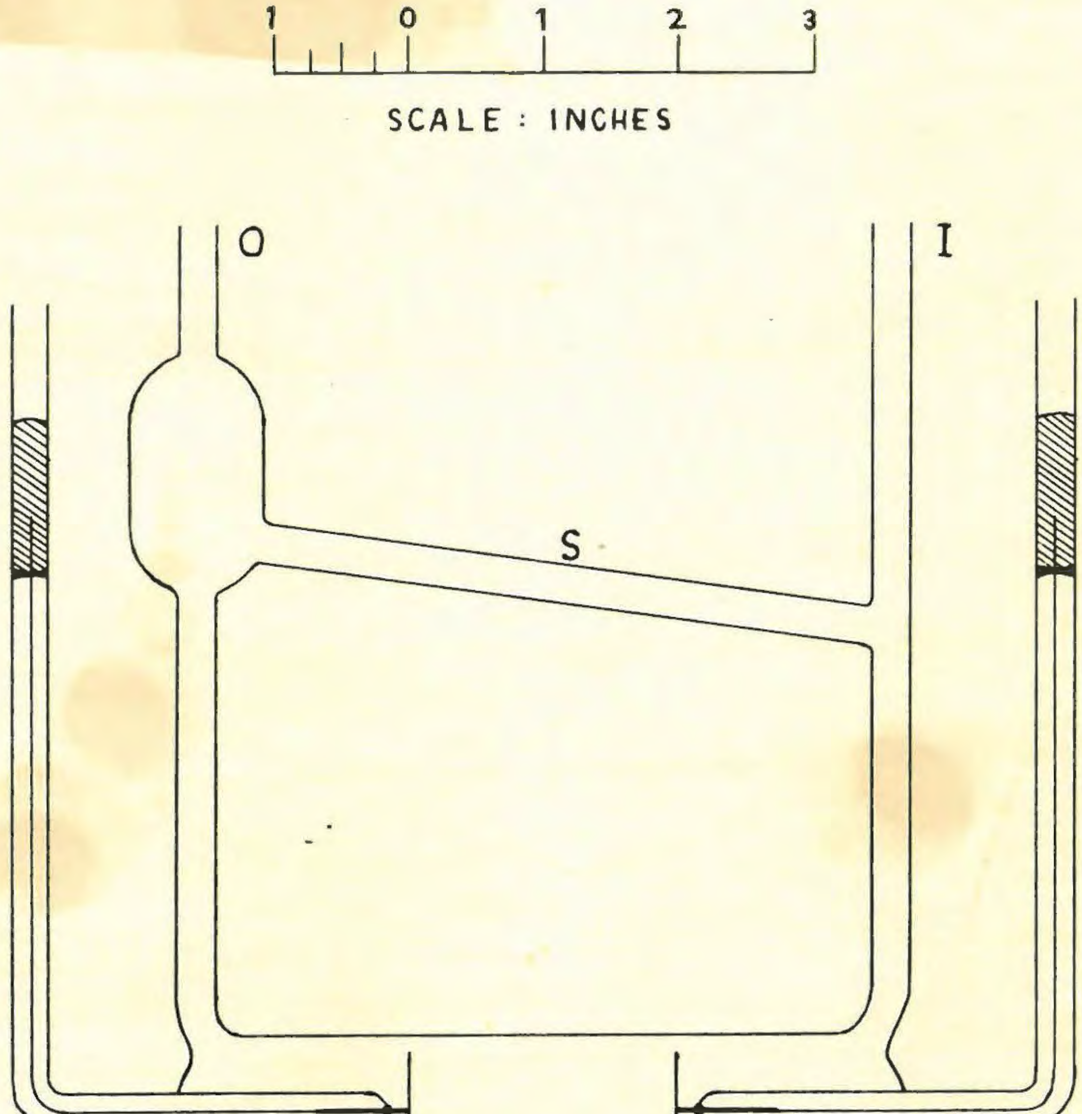


FIG. XII CELL 4

Cell II is of type (i). It had previously been used by G. McP. Malan, who had platinized the electrodes lightly (7 coulombs per electrode) using the solution recommended by Jones and Bollinger (40).

Cell III was of type (ii), with a cell constant of about 1. The electrodes were lightly platinized (6 coulombs per electrode) using the Jones and Bollinger solution. This cell was used for the first part of the work, until one of its electrode seals cracked.

Cell IV is similar to Cell III. Experiments were carried out in this cell with the electrodes platinized and unplatinized, but it was eventually used (after Cell III broke) with the electrodes unplatinized.

Cell V is of type (ii), but with a cell constant of about 0.1. The electrodes were platinized to 6 coulombs per electrode. This cell was never very satisfactory, as it gave erratic readings, and was not used for measurements on KCl solutions. It was however used for experiments on the conductivity of water.

The weight burette

The weight burette consists of a 12 ml. bulb with a tap at the top and a standard A7 Quickfit ground-glass joint, tapering to a fine jet, at the bottom. As a burette long enough to be filled directly from a flask would be very unwieldy, there is a separate "filling tube". This is a tube about 6 inches long, with an A7 Quickfit ground-glass joint at one end; it was used only when filling the burette. There is also a cap which was placed over the jet while weighing, to prevent evaporation.

As the tap is at the top of the burette, the solution never came in contact with it, and was therefore not contaminated by grease. (The burette was filled by connecting a vacuum pump to the top and sucking up solution through the filling tube until the bulb was full, taking care not to wet the tap.)

The "wet box"

The "wet box" is a 2 x 2 x 1½ ft. box in which the relative humidity was maintained at nearly 100%; the filling, etc., of the weight burette was done in it. The high r.h. was maintained by having "curtains", which were always kept moist, on the back and sides of the box. The front, which is detachable, has two 6 inch square openings covered with rubber sheet: in each sheet is a hole through which the operator can insert his arm up to the elbow. There is a glass panel in the top of the front.

Flasks

Various flasks, ranging in size from 50 ml. to 1 l., were used; all of them were fitted with Quickfit ground-glass joints and stoppers.

C. PURIFICATION OF MATERIALS

Potassium Chloride

Recrystallization: 500 g. of "AnalaR" G.R. potassium chloride was recrystallized three times from water, the mother liquor being separated by decantation. The first two recrystallizations were done in a Pyrex flask using distilled water, the third using conductance water in a large platinum dish, stirring with a platinum spatula. The product was dried in a platinum dish in an electric oven, first at 120°C, then at 250°C.

Two batches were prepared in this way; these will be designated I and II.

Fusion: The generally-accepted method of removing the last traces of water from KCl is fusion. Gledhill (1) and Festenstein (41) fused their KCl in air; but on examining some of Festenstein's KCl, it was found to be faintly yellow, and gave a red colour when tested with phenolphthalein. It was therefore decided to do the fusion in an atmosphere of nitrogen.

Some experimental fusions were done with the KCl in a platinum boat in a silica tube through which a stream of pure nitrogen was passing. This method was eventually abandoned, partly because of the small quantity it was possible to fuse each time, partly because of the difficulty experienced in removing the fused salt from the boat without touching it.

In the second method, the KCl was placed in a platinum crucible at the bottom of a large quartz test-tube, which was closed at the top with a closely-fitting Pyrex glass cap. Nitrogen, which had been purified by passing over heated copper turnings and phosphorus pentoxide, was passed into the test-tube at a rapid rate through a tube sealed in the top of the cap, and escaped to the atmosphere through the space between the cap and the test-tube.

In the first fusion (IA) the crucible was heated by clamping the quartz tube vertically in an electric furnace. The product was water-white, but a crust of unfused KCl was left at the top of the crucible. The second attempt by this method was unsuccessful, as the salt did not fuse at all, even after two hours. IB and IC were eventually fused by heating the tube in an oxygen-coal-gas flame. This method was very much quicker than the other, but on examining the melt it seemed to be very faintly yellow in the centre. However, after removing the KCl from the crucible, all the large white crystals were sorted out, and tested with phenolphthalein; as no red colour could be detected, it was decided to use the product.

As fusion in the flame was not entirely satisfactory, the electric furnace was again used for batch II, with some modifications: firstly, a "Variac" transformer was used to keep the line voltage up to its rated value; secondly, a metal shield was suspended half-way down the quartz tube to cut down heat losses by convection and radiation. The ideal material for this shield would have been platinum, but a piece of suitable size was not available, and nickel was used instead. With these precautions the KCl fused completely. Unfortunately the nickel became covered with a greenish-black deposit which did not adhere firmly, and in II C some of this was obviously dislodged, for there was a clearly defined yellow patch in the centre of the melt. II C was therefore discarded, and the KCl from II A and II B (which was water-white) was used for the rest of the work.

In all cases it was necessary after fusion to distort the crucible to remove the KCl, and even then great difficulty was experienced. A small stainless-steel spatula proved to be of great assistance in dislodging the crystals.

(Note: Addink (42), while working on the degree of imperfection of crystals, investigated the removal of water from KCl. He states: "Heating the crystals up to a temperature of 550°C for half an hour in very pure and dry nitrogen was sufficient. Heating to a temperature of 900°C is not necessary to expel all water".

It appears that fusion of KCl to remove traces of water is not only laborious, but quite unnecessary.)

Water

Some time was spent in designing and constructing a still for the preparation of conductance water. This has already been described elsewhere (see reprint at back of book).

Air

Air from a compressor was passed through: a series of tubes containing soda-lime, to remove carbon dioxide; a U-tube containing meta-phosphoric acid, to remove ammonia; another tube containing soda-lime; two bubblers (A and B) filled with conductance water, to saturate the air with water vapour at 24°C; and the potash bulb filled with conductance water in the thermostat (see p. 26), to saturate the air with water vapour at 25°C.

As the bubbling rate affects the conductivity of water, a uniform bubbling rate is essential; for this reason a constant pressure was maintained on the inlet side of the purification train. The regulating device was a bubbler filled with mercury, with an outlet to the atmosphere, through which a small amount of air was allowed to escape; the pressure was thus maintained constant at a value depending on the depth of immersion of the inlet tube.

D. POLARIZATION CORRECTION

In order to minimize adsorption on the electrodes of the conductance cell, it was decided to make the platinization very light, and to correct for polarization effects by a suitable extrapolation. This is contrary to common practice, for most people platinize so heavily that the variation of resistance with frequency is either negligible, or so small that the resistance at the higher frequency can be taken as correct.

Galvanic polarization was studied in some detail by Jones and Christian (43), using a special cell with movable electrodes. To correct for it, they recommend plotting R v. $f^{-\frac{1}{2}}$ (where R = resistance of cell, and f = oscillator frequency); the graph should be a straight line, and the true resistance of the cell is obtained by extrapolating to $f^{-\frac{1}{2}} = 0$. However, it was found in this department (see e.g. Goddard (44)) that the graph is not a straight line, and the extrapolation is therefore unsatisfactory. There were indications that plotting R v. f^{-1} gave a straight line, and it was decided to test this over a wide frequency range, using a cell with unplatinized electrodes, before commencing work on the conductivities of KCl solutions.

Experimental

In order to extend the frequency range of the conductance bridge, an oscillator and amplifier were borrowed from another bridge which was being built at the time to study polarization. These were connected in parallel with the built-in units, so that either could be used as required. As the new amplifier was untuned, to prevent excessive a.c. pick-up it was necessary to install a band-pass filter, which cut off the lower frequencies. As mentioned earlier (p. 62), the normal cell connecting leads were replaced by coaxial cable. With these modifications, it was possible to take readings with a precision of 0.003% at 5000 c.p.s., and of 0.01% at 9000 c.p.s. The decrease in sensitivity at higher frequencies was probably due to the 578-B bridge transformer, which is designed to work in the range 20 to 5000 c.p.s.

Before commencing the experiment, the electrodes of Cell IV were cleaned by electrolysing concentrated hydrochloric acid. One litre of approximately 0.06 N KCl solution was prepared, and was used throughout the experiment. The resistance of this solution in Cell IV was measured, using the standard procedure described in Section E. After the reading had been taken (at 1800 c.p.s.), the bridge was left switched on, and the resistance measured at intervals until it was constant (there was a slight drift due to heating effects). Readings were then taken over the range 350 to 9000 c.p.s., and later over the range 900 to 3500 c.p.s. in more detail. A General Radio decade condenser box (type 219-M) was used as the additional capacity in the measuring arm. The resistance at 1800 c.p.s. of several aliquots was measured, but the resistance over the range of frequencies was measured only once, as it did not seem likely that the polarization correction would change appreciably in the short time between readings.

The electrodes of the cell were then platinized (7½ coulombs per electrode), using the solution recommended by Jones and Bollinger (40), and rinsed well with conductance water. Another set of readings was taken in the same way as before.

Results

It has recently been found that the decade condenser box used in taking readings introduced appreciable errors when the 0.1 microfarad decade was used. As a result, the measurements with bright electrodes are not accurate at frequencies below 900 c.p.s., and are not recorded here.

Fig. XIII shows the graph R v. f^{-1} over the range 900 to 9000 c.p.s. Lines (1) and (2) represent the readings with bright electrodes, line (3) the readings with platinized electrodes. In (1) the readings were plotted without correction, in (2) the $p^2C^2R^3$ correction (see p. 61) was applied: this correction was negligible in (3).

The same points against $f^{-\frac{1}{2}}$ are shown in Fig. XIV. It can be seen that this definitely does not give a straight line.

In Fig. XIII (2) and (3) are straight lines, but (1) curves up at lower frequencies. The extrapolated values of (1) and (2) are nearly the same (102.86 and 102.87 ohms respectively), but are lower than the extrapolated value of (3) (102.904 ohms). If anything, one would have expected (1) and (2) to extrapolate to a higher value, as the platinum deposited on the electrodes would tend to decrease the cell constant. It therefore seems that plotting R v. f^{-1}, although an improvement on R v. $f^{-\frac{1}{2}}$, still does not give an accurate extrapolation. However, as the difference between (1) and (3) is only 0.04%, and as the total polarization correction in actual measurements would always be less than 0.1%, it was decided to determine the polarization correction by plotting R v. f^{-1} and extrapolating to $f^{-1} = 0$.

When Cell IV was first used with 0.01 D KCl solution, it was found that plotting R v. f^{-1} did not give a straight line (Fig. XV (1)); the linearity was improved only at lower frequencies by plotting against $f^{-\frac{1}{2}}$ (line (2). Since Cell III had given a straight line with a smaller slope when plotting R v. f^{-1}at this concentration (line (3)), although the electrodes were not as heavily platinized, it appeared that the platinization of Cell IV was not as effective as that of Cell III.

At this stage, as the effect of platinization appeared to be somewhat erratic, it was decided to use Cell IV with unplatinized electrodes. The platinization in Cell II appeared to be satisfactory, and as the correction with bright electrodes would have been very large, it was decided to use it as it was.

There is a marked difference between the R v. f^{-1} graphs obtained at different concentrations with Cells II and IV. With Cell IV the graph is a straight line whose slope remains almost constant over a wide range of concentrations (i.e. ignoring Parker effect: see note below). With Cell II the graph is a straight line at higher concentrations, but becomes curved at lower concentrations (Fig. XVI). However, as the correction is very small, the uncertainty in extrapolation is less than 0.01%.

Note: Parker effect in Cell IV first became apparent when measuring the conductivity of 0.000784 N solutions, and was shown by an upward turn in the extrapolation curve at higher frequencies (see Fig. XVII). To confirm that this was due to Parker effect, some of the solution was poured out, so that the tube S was empty (thus effectively making an ordinary Jones cell); the upward curve then disappeared.

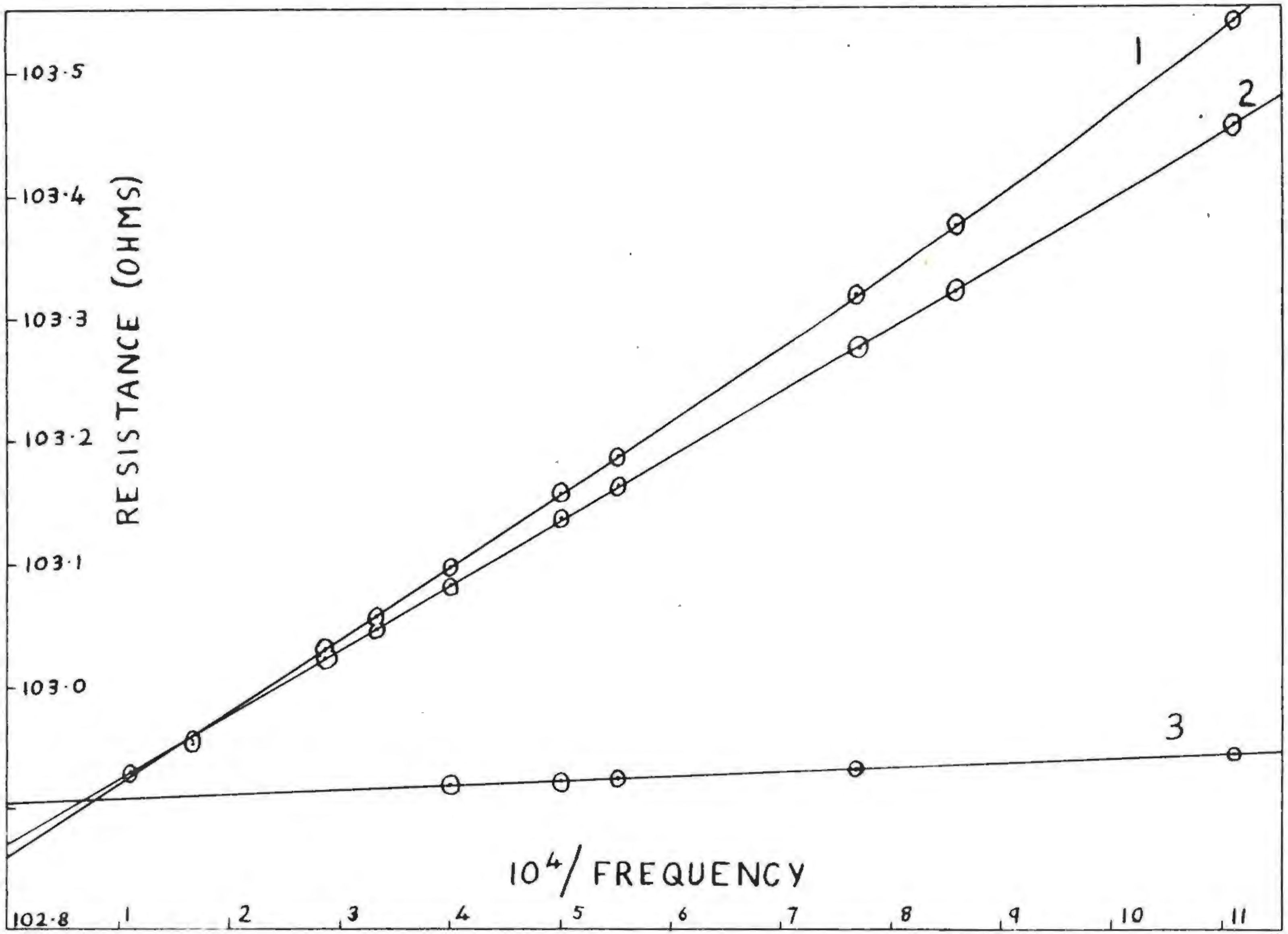
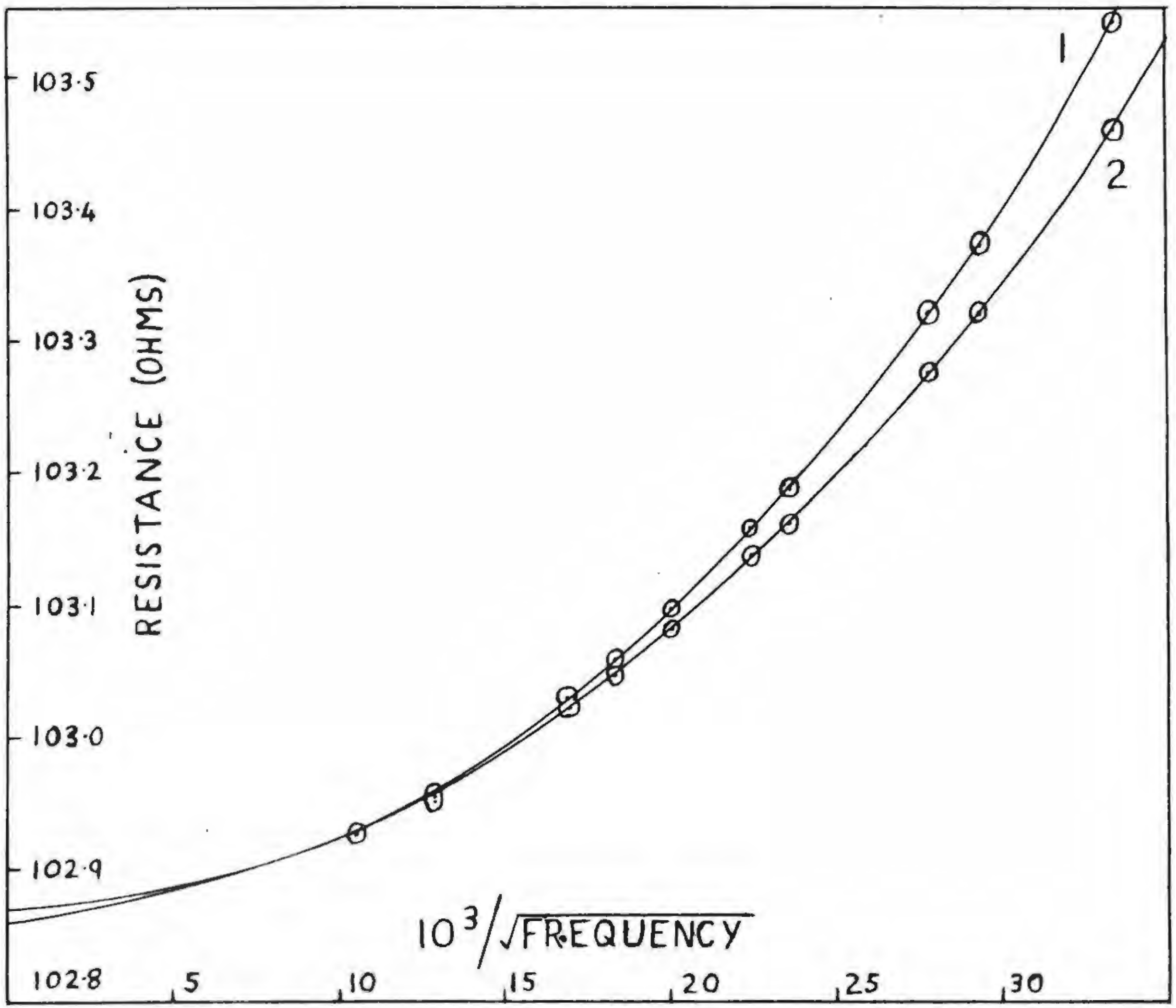

103·5
103·4
103·3
103·2
103·1
103·0
102·8
RESISTANCE (OHMS)
1
2
3
4
5
6
7
8
9
10
11
10^4/ FREQUENCY
1
2
3

FIG. XIII



1
2
103·5
103·4
103·3
103·2
103·1
103·0
102·9
102·8
RESISTANCE (OHMS)
5
10
15
20
25
30
$10^3/\sqrt{\text{FREQUENCY}}$

FIG. XIV

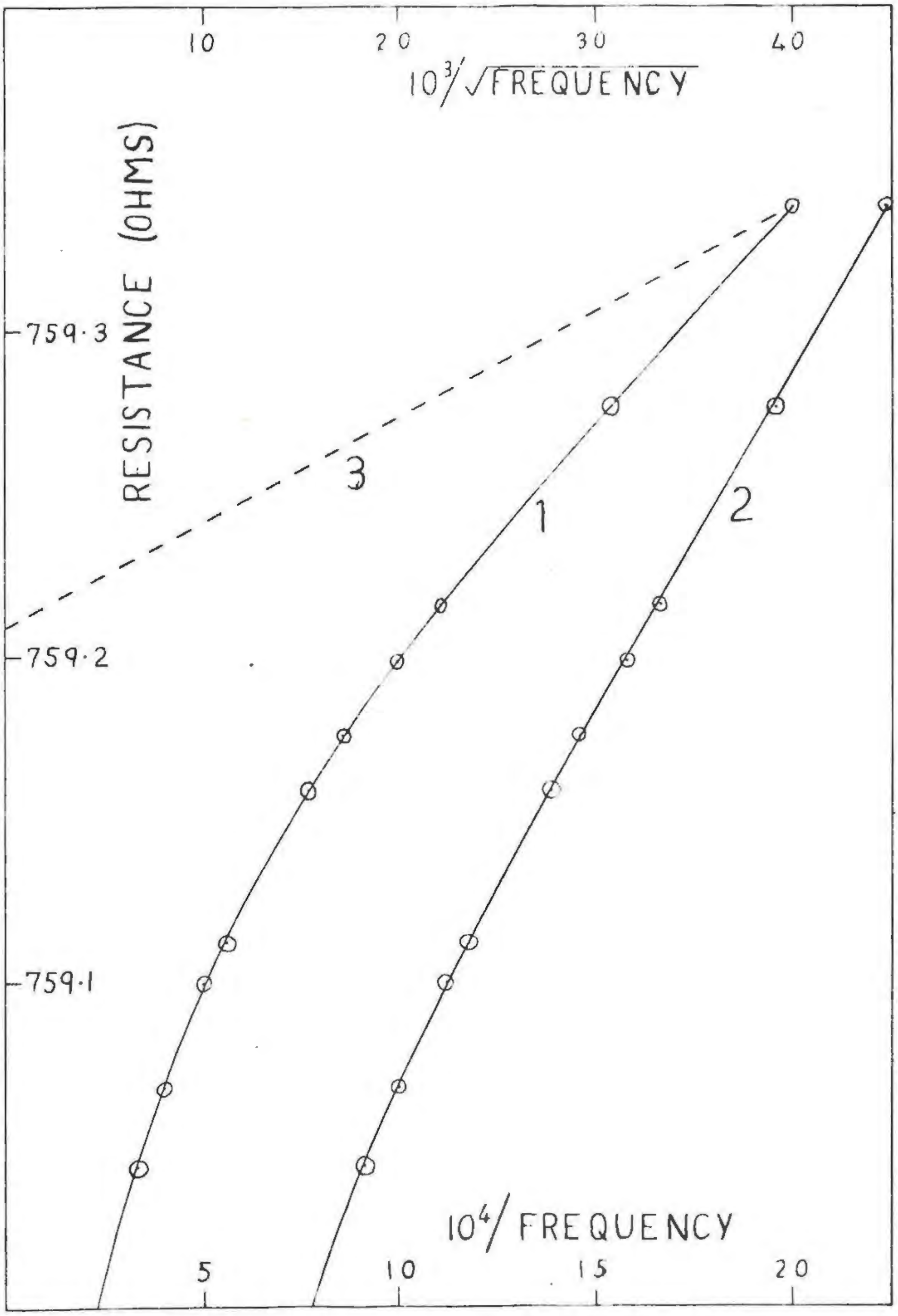

10
20
30
40
$10^3/\sqrt{\text{FREQUENCY}}$
RESISTANCE (OHMS)
759·3
759·2
759·1
3
1
2
10^4/ FREQUENCY
5
10
15
20

FIG XV

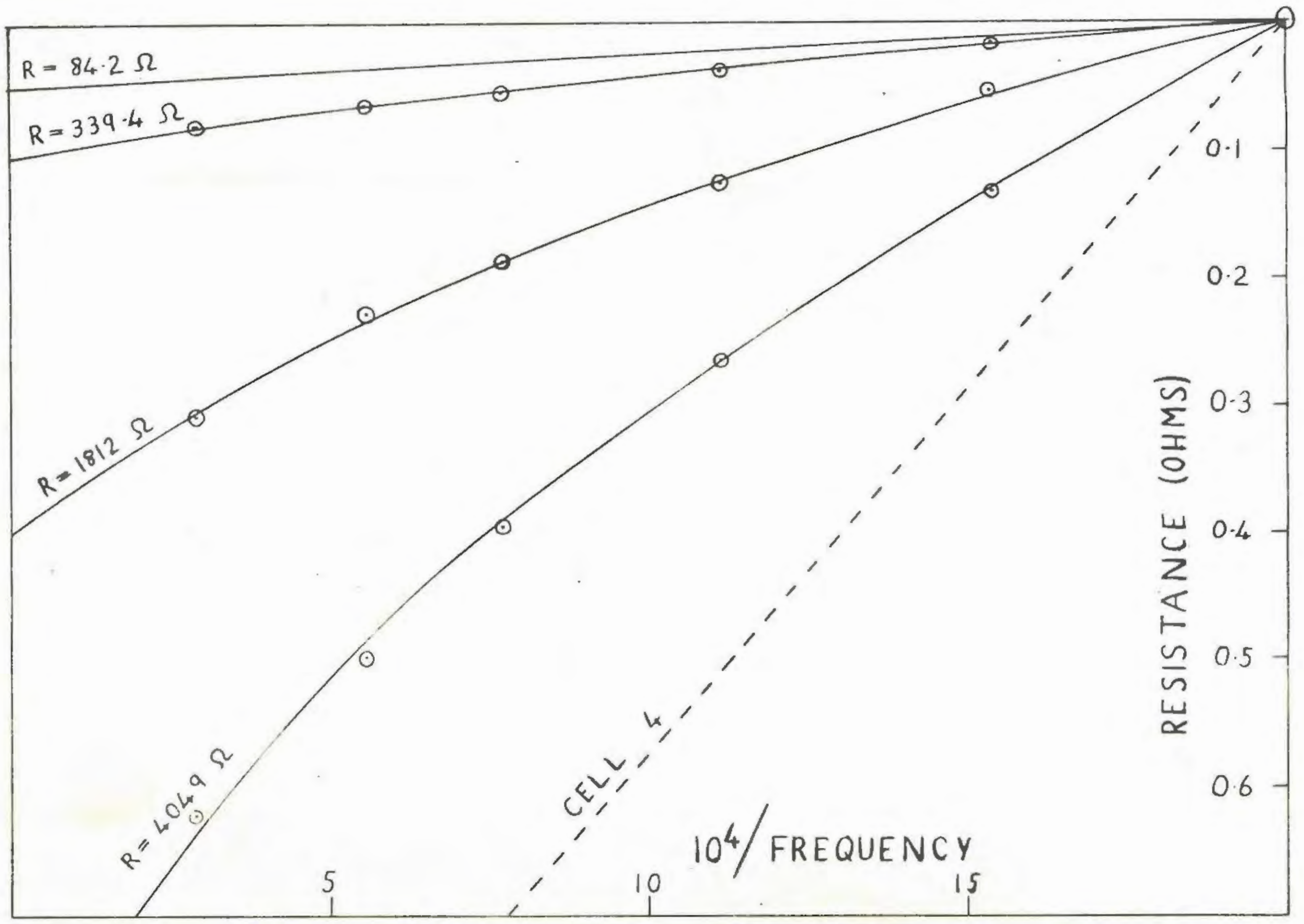

R = 84·2 Ω
R = 339·4 Ω
R = 1812 Ω
R = 4049 Ω
CELL 4
10⁴/FREQUENCY
5
10
15
RESISTANCE (OHMS)
0·1
0·2
0·3
0·4
0·5
0·6

FIG. XVI

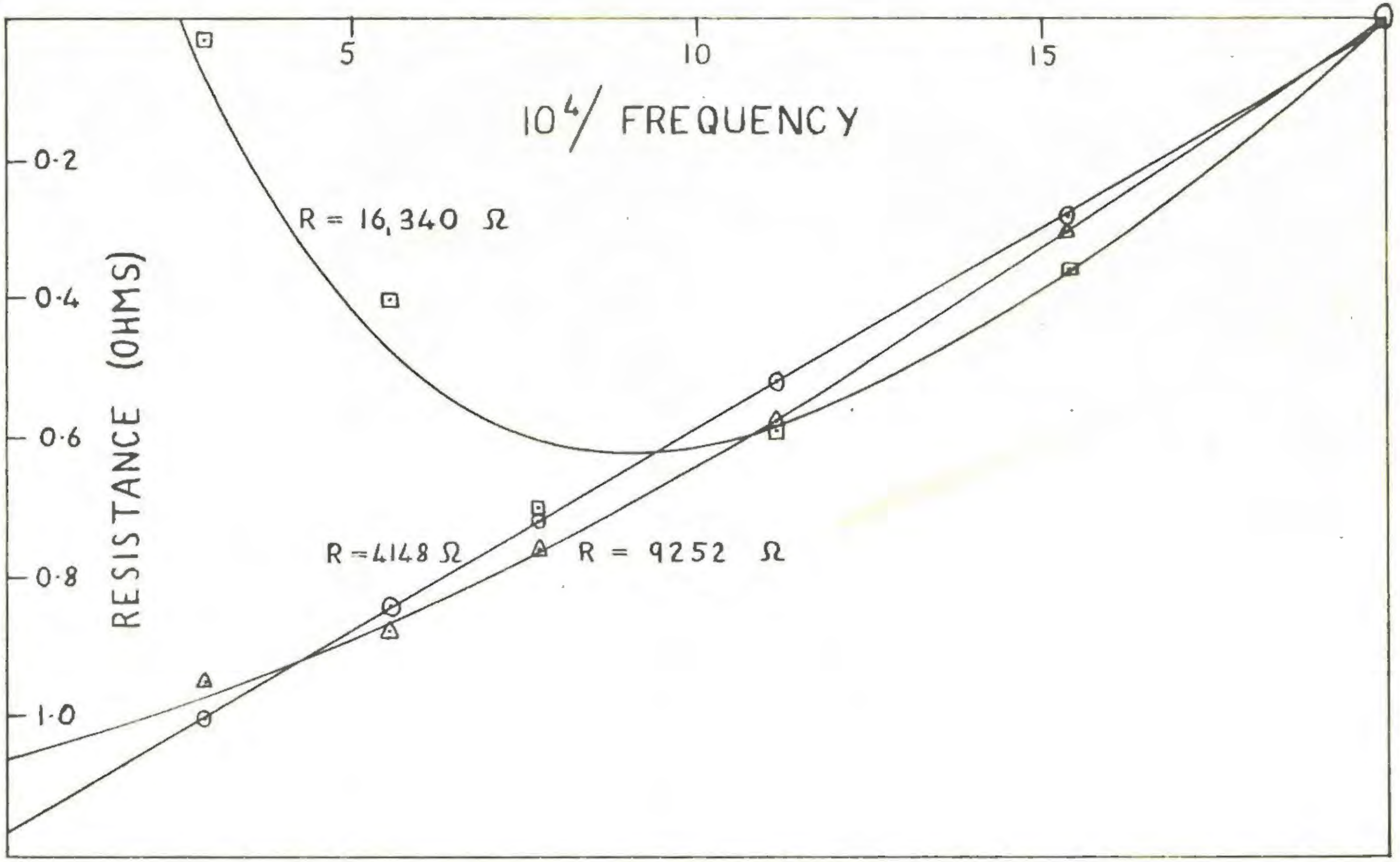

5
10
15
10^4/ FREQUENCY
0·2
0·4
0·6
0·8
1·0
RESISTANCE (OHMS)
R = 16,340 Ω
R = 4148 Ω
R = 9252 Ω

FIG. XVII

E. EXPERIMENTAL SECTION

Weighing of Potassium Chloride

Richards (45) states: "Potassic chloride, although not so hygroscopic as some other salts used in similar researches, is nevertheless far too hygroscopic to weigh safely when exposed to the air of the balance room. Its tendency to attract water was seen in perceptible crackling when the tube containing fused salt was opened in the moist atmosphere of the beaker to be used for the solution of the salt."

In spite of this statement, none of the workers measuring the conductivities of KCl solutions protected the salt from the atmosphere while weighing, although Shedlovsky (46) used a "Richards bottling apparatus" (47) for work on other salts.* However, while experimenting with fusions in the platinum boat (see p. 77), the crackling mentioned by Richards was observed when removing the boat from the tube, and it was decided to investigate the effect. KCl was fused in pure nitrogen and, using a "Richards bottling apparatus", was weighed on B II before and after exposure to the atmosphere of the room. The results were not very reproducible, but showed that the KCl did not absorb more than 0.02% moisture; it seemed that the crackling was associated with changes

* In a private communication, Shedlovsky states that he used a Richards bottling apparatus for all his work, including KCl.

in temperature rather than changes in humidity. It was therefore decided to weigh the salt in an open container, provided the relative humidity was less than 75% (calcution showed that the relative humidity over a saturated solution was over 80% at room temperature). The work of Addink (48) confirms the fact that this procedure introduced no error, for his results show that although fused KCl crystals do absorb about 0.02% water when stored over a saturated solution of ammonium chloride, it takes about three days to absorb 0.01%.

All weighings of KCl were done on B I using a small silver dish (weight 1½ g.) and tare; in no case was the weight of KCl less than 0.2 g.

Experiments with the "wet box"

Preliminary experiments with the weight burette showed that there was a loss of about 2½ mg. of water when running the solution from the burette into a weighing bottle: in order to prevent this the "wet box" was built. However, it was found that even when the transfer was carried out in the box there was still a loss of about 1 mg. As the relative humidity in the box was nearly 100 %, this was at first puzzling; but a likely explanation is that currents of warm air from the arms of the operator would not be saturated with water vapour, and would cause evaporation.

Experiments were then carried out in which the arms of the operator were covered with a film of moisture by wiping with a damp cloth before using the burette. In a number of trials the maximum loss of weight was 0.4 mg. and in one case there was an increase in weight of 0.1 mg. As the change was less than 0.004%, this technique was used in making up solutions.

Preparing solutions

Direct method: The KCl was weighed into a 1 litre Pyrex flask, and the weight of water required to make a solution of exactly the right concentration was calculated. Slightly less than this amount was added, using as a guide a series of rough calibration marks on the side of the flask. It was then weighed on B III to 0.1 g., and the rest of the water (less than 10 ml.) added from a clean 10 ml. measuring cylinder, which was used solely for this purpose. It was then weighed again to 0.01 g., and was normally within 0.1 g. of the correct weight; the correction for the difference was applied when calculating the results.

The solution was allowed to warm up to 24°C in the c-t room before it was used. After readings had been taken in both cells, the remaining solution was poured out, and the flask left to drain for about 10 seconds; it was then ready for the next solution.

When the concentration was changed, the flask was first "seasoned" by making up a solution of roughly the right concentration, using B II and B III. This solution was also used to rinse out the cells.

Indirect method: When measuring the conductivity of dilute solutions, the amount of KCl required to make a flaskful of solution was too small to be weighed with an accuracy of 0.01% (e.g. for a 0.000049 N solution less than 3 mg. of KCl was required). For this reason an "intermediate solution" (i.s.) was prepared, of such a concentration that 12 ml. (the volume of the weight burette) contained enough KCl to make up 800 ml. of dilute solution. Each i.s. was used for the preparation of only one dilute solution. Generally the weight of KCl used for an i.s. was only about 0.5 g., and hence the volume of i.s. which was prepared varied considerably; for a 0.004900 N solution it was about 30 ml., but for a 0.000049 N solution it was about 800 ml.

About 0.5 g. of KCl was weighed into a clean dry flask of convenient size, which was then weighed on B II or B III. Conductance water was run in from a clean burette (kept solely for this purpose), taking care not to wet the ground-glass joint. When the total weight was less than 100 g., the flask was placed in the c-t room, and weighed on B II after it had warmed up to 24°C; when it was more than 100 g., it was weighed on B III, and then placed in the "wet box" to warm up. In both cases care was taken not to wet the ground-glass joint until the temperature of the contents was 24°C, otherwise the pressure which developed loosened the stopper and forced out some solution.

In the case of the 0.000049 N solution, the i.s. was prepared in a 1 litre flask by the direct method described on p. 89.

The dilution of the i.s. was done as follows: some time before it was proposed to start work, all the apparatus was placed in the "wet box", the vacuum pump was connected, and the filling tube fitted to the burette. When the air in the box had become saturated with water vapour again, the arms were wiped with a damp cloth and inserted through the holes in the front, and the i.s. was thoroughly shaken up. The burette was rinsed once with the i.s., filled to just below the tap, the filling tube and vacuum pump connection removed, and the cap replaced; it was then removed from the box, wiped dry with a clean cloth, and weighed on B II. After replacing it in the box, the cap was removed and the solution transferred to the 1 litre flask, running it down the side to avoid splashing, but not over the ground-glass joint. The weight of KCl was then calculated and the solution made up as in the direct method.

This technique was checked at concentrations of 0.0049 N and 0.003969 N by making up solutions by both the direct and indirect methods, and comparing the conductivities. It was found that there was no significant difference between the methods (see results in Appendix).

Note: A certain amount of care was necessary when removing and replacing the cap and filling tube of the weight burette in order to avoid getting solution on the ground-glass joint; if this happened, a ring of liquid formed at the top of the joint, and evaporated while weighing.

Cell lead resistance

The lead resistances of Cells II, III, IV and V were measured by filling the cells with clean dry mercury and measuring the resistance by the method described on p.68. The resistance of the solution in Cell I was always very high, hence the lead resistance correction was negligible.

Conductivities of solutions

Cells III and IV: Some difficulty was experienced at first in getting reproducible results with Cell III, and it was some time before the trouble was traced to:

(i) a bubble lodging in the lower end of tube S, which caused the cell to have a variable resistance depending on the size of the bubble. A tap, opening to the atmosphere, was sealed into the glass tube connecting tube I (Fig. XII) to coil A; by opening this tap momentarily just before measuring the resistance, the excess pressure in coil A was released, thus removing the bubble.

(ii) Condensation of water in the cool parts of the connecting tube mentioned above. Because of this, the air going into the cell was not saturated with water vapour, and removed water from the solution; this caused the conductance to increase by about 0.003% per hour. Although various attempts were made, there did not seem to be a simple way of preventing this. Eventually it was decided to keep the time and rate of bubbling constant, so that the change in concentration would be the same for all solutions, including those used for cell constant determinations; the errors would therefore cancel out when calculating conductivities.

The standard procedure finally adopted was as follows:

Switch off room fan, rinse cell once with fresh solution, fill to mark[1], put on connecting tube and guard tube, and place cell in thermostat. Pass air through at the rate of one bubble in two seconds[2] (measured on Bubbler B in purification train) for 20 minutes, then at 5 bubbles per second for 2½ hours. Turn off stirring, remove bubble in tube S, wait 3 minutes, then take reading on bridge[3]. Note the thermostat temperature.

Notes

1. The mark was about ½ inch above the highest point of tube S.

2. Fast bubbling is obviously undesirable until the temperature of the solution is the same as that of the air from the purification train. On the other hand, on one occasion without stirring, some small bubbles formed in the cell between the electrodes. Calculation showed that 1 bubble in 2 seconds would not cause a significant change in concentration, but would still stir the solution to some extent.

3. In general readings were taken at only one frequency, with ratio arms direct and reversed. For the first part of the work the frequency was 1800 c.p.s., but for the more dilute solutions it was changed to 900 c.p.s.

Cell II: This cell gave reproducible readings, but heating effects were noticeable in the more concentrated solutions, even though the bridge voltage was only 0.5 v. e.g. the conductance of a 0.01 D solution increased by 0.03% if the oscillator was left on for a long time. Readings were therefore taken as soon as possible after switching on the bridge. The standard procedure was: Switch off room fan, rinse cell once with fresh solution, fill to the mark and place in thermostat with air passing through tube B. After 1 hour divert air to bubble through solution (i.e. through tube A), and adjust to 5 bubbles per second, measured on bubbler A. Continue bubbling for 3 hours, switch on bridge units, divert air from tube A to tube B, and take reading 4o seconds later. Note thermostat temperature.

Note: The mark in this cell was about 2 inches from the top. Readings were always taken at 900 c.p.s.

In the case of the 0.000049 N solutions, where the correction for the conductivity of water was large (over 1%), the standard procedure was modified. Instead of taking readings after a standard time, the resistance was measured at intervals until it reached a maximum value and began decreasing again. As the conductivity began increasing at the rate of 1 to 2 x 10^{-10} ohm^{-1} cm.^{-1} per minute as soon as the stirring was stopped, in order to work quickly no readings were taken with the ratio arms reversed; a correction was applied later to these readings. It would have been better to have adopted this procedure for the three lowest concentrations (0.000441 N, 0.000196 N and 0.000049 N), though this was not realized at the time. However, in the case of the 0.000049 N solutions a comparison showed that there was never a difference of more than 0.01% between the results obtained by the two standard procedures, so that it is unlikely that this caused any significant error.

Routine determination of polarization correction

The resistance was determined at various frequencies as described in Section D, but not over such a wide range. Normally readings were taken at 500, 650, 900, 1300 and 1800 c.p.s., but the additional oscillator was left connected, and in some cases where the graph curved up at low frequencies readings were taken at 3500 c.p.s. as well (with the bridge amplifier set at 2000 c.p.s.).

In general the polarization correction was determined only once for each concentration.

Because it was found that even line (2) in Fig XIII curved up at lower frequencies, the $p^2C^2R^3$ correction was not used. It was negligible except when measuring the resistance of concentrated solutions in Cell IV at low frequencies, and then only the readings at higher frequencies were used to determine the polarization correction.

Conductivity of water

The conductivity of the water used for making up solutions was measured in Cell I, which was used only for this purpose; the bubbling rate was the same as that for Cell II. As the resistance of the cell was outside the range of the bridge, the cell was shunted with a non-inductive 10,000 ohm resistance (General Radio type 500-J). Unlike measurements on solutions, readings were taken with the air bubbling through the cell.

It was shown by P.K. Faure (38) that the conductivity of water in a conductance cell decreases as the flow of carbon-dioxide-free air is increased (the drift in resistance mentioned earlier is due to this effect). Bubbler A has a lower bubbling rate than B (i.e. the volume of the bubble is larger). The amount of air flowing through Cells II and IV was respectively 5 bubbles per second counted on A and 5 bubbles per second counted on B; therefore the flow of air through Cell II was greater than that through Cell IV, and the correction for water conductivity in the two cells was different. The difference was determined by measuring the conductivity of water from the same flask in Cells I and V, with the appropriate bubbling rate for each cell.

Note: The cell constant of Cell I was determined by measuring the conductivities of approximately 0.000049 N solutions in Cells I and II; at this concentration errors due to lead resistance and polarization were negligible.

F. RESULTS

All results are based on the value of Jones and Bradshaw (49) for the conductivity of 0.01 D KCl solution i.e. a 0.01 D KCl solution contains 0.745263 g. KCl per 1000 g. solution, and has a conductivity of 0.00140877 $ohm^{-1}\ cm^{-1}$.

All concentrations are expressed in gram-equivalents per litre of solution (i.e. normality).

In making up solutions, Li and Fang's (50) formula for the density d of KCl solutions was used:

$$d = 0.99707 + 0.00635 f \quad \text{g. per ml.}$$

where f = weight % of KCl.

The atomic weights were taken as: K = 39.096, Cl = 35.457; hence KCl = 74.553.

The table on the next page shows the values of the equivalent conductivities obtained with Cells II, III and IV. Columns III and V give the deviations from the equation proposed by Davies (35) for the equivalent conductivities of KCl solutions:

$$\Lambda = 149.92 - 93.85 c^{\frac{1}{2}} + 50 c$$

where c = concentration in gram-equivalents per litre. This empirical equation was calculated from the experimental results of Shedlovsky (33), which are probably the most accurate at present.

$c \times 10^4$	Equiv. cond. Cells III & IV	Dev. from Davies equn.	Equiv. cond. Cell II	Dev. from Davies equn.	Diff. between cells
0.49	-	-	149.83	+0.57	-
1.96	148.69	+0.07	148.87	+0.25	0.12%
4.41	147.93	-0.04	148.06	+0.09	0.09%
7.84	147.29	-0.04	147.39	+0.06	0.07%
12.25	146.68	-0.02	146.76	+0.06	0.05%
17.64	146.05	-0.02	146.11	+0.04	0.04%
24.01	145.40	-0.04	145.45	+0.01	0.03%
31.36	144.80	-0.02	144.83	+0.01	0.02%
39.69	144.22	+0.01	144.24	+0.03	0.02%
49.00	143.67	+0.08	143.66	+0.07	0.01%

G. DISCUSSION OF RESULTS

The most striking feature of the results is the large discrepancy between Cell II and Cell IV, and in view of the reasonably close agreement between the results of Cell IV and the Davies equation, it appears that Cell II is at fault. The cause of the error is not clear, but the following possibilities were considered:

Error in the lead resistance correction: This could not be checked experimentally, as G. McP. Malan was using the cell at the time. However, calculation shows that it cannot explain the deviations observed.

Parker effect: The cell was specially designed to be free from this error, but there is still the possibility that capacities between the lead wires and the solution may cause errors. However, measurements of the resistance of Cell I filled with conductance water at different frequencies showed that the resistance was indepedent of frequency. As any error due to Parker effect would be very large under these conditions, it seems that the cell is free from this effect.

Platinization: In view of the trouble experienced with platinization in the early stages of the work, and also of the difference between the extrapolation graphs of Cells II and IV, it is possible that the error is due to faulty platinization. However, other workers have used platinized electrodes and obtained consistent results.

Adsorption: Let it be assumed that adsorption of KCl took place on the platinized electrodes, but that a certain amount of this was desorbed when the cell was stirred. Readings were always taken when the cell was stirred, but the solution was changed after the cell had been standing for some time. Under these conditions it is obvious that the concentration of KCL in solution while taking readings will be higher than the concentration in the freshly-filled cell.

This theory is not borne out by the actual readings, as the conductance of the solution always increased when the stirring was turned off.

In conclusion it is recommended:

(i) that further work be done on the determination of the polarization correction.

(ii) that the cause of the inaccurate readings with Cell II be investigated; and that until this has been done, cells of this type should not be used for accurate work.

APPENDIX

Calibration of bridge resistances

Ten thousands decade

Setting	Corr. ohms (1949)	Corr. ohms (1951)	% diff.
1	+8.6	+9.1	0.005
2	+13.7	+13.9	0.001
3	+20.3	+20.4	0.000
4	+28.7	+28.8	0.000
5	+37.5	+37.3	0.000
6	+45.7	+45.1	0.001
7	+51.4	+50.4	0.001
8	+59.5	+58.6	0.001
9	+69.5	+68.2	0.001
10	+78.2	+77.1	0.001

Thousands decade

Setting	Corr. ohms (1949)	Corr. ohms (1951)	% diff.
1	+0.78	+0.73	0.005
2	+1.62	+1.46	0.008
3	+2.99	+2.72	0.009
4	+3.64	+3.35	0.007
5	+4.66	+4.35	0.006
6	+5.96	+5.62	0.006
7	+6.67	+6.29	0.005
8	+7.65	+7.25	0.005
9	+8.69	+8.29	0.004
10	+9.78	+9.44	0.003

Hundreds decade

Setting	Corr. ohms (1949)	Corr. ohms (1951)	% diff.
1	+0.113	+0.107	0.006
2	+0.223	+0.211	0.006
3	+0.370	+0.350	0.007
4	+0.472	+0.447	0.006
5	+0.522	+0.488	0.007
6	+0.604	+0.563	0.007
7	+0.768	+0.719	0.007
8	+0.879	+0.825	0.007
9	+1.030	+0.966	0.007
10	+1.199	+1.130	0.007

Tens decade

Setting	Corr. ohms (1949)	Corr. ohms (1951)	% diff.
1	+0.0208	-	-
2	+0.0443	-	-
3	+0.0656	-	-
4	+0.0852	-	-
5	+0.1062	+0.1016	0.009
6	+0.1330	+0.1285	0.008
7	+0.1555	+0.1497	0.008
8	+0.1784	+0.1719	0.008
9	+0.1982	+0.1918	0.007
10	+0.2230	+0.2166	0.006

Units decade

Setting	Correction ohms (1949)
1	+0.0017
2	+0.0002
3	-0.0005
4	+0.0018
5	+0.0021
6	+0.0024
7	+0.0017
8	+0.0014
9	+0.0008
10	-0.0019

Tenths decade

Setting	Correction ohms (1949)
1	+0.0006
2	+0.0005
3	+0.0007
4	+0.0009
5	+0.0012
6	+0.0015
7	+0.0018
8	+0.0023
9	+0.0028
10	+0.0030

The slidewire

Note: The calibration below is set out in the same way as logarithm tables. The units are ohms x 10^{-4}. The values given are actually twice the measured resistance (see p.56).

	0	1	2	3	4	5	6	7	8	9
0	-	-	-	-	-	-	0000	0012	0023	0036
1	0048	0060	0072	0086	0098	0109	0121	0133	0146	0158
2	0170	0182	0194	0206	0218	0230	0242	0254	0266	0279
3	0292	0304	0316	0328	0340	0352	0364	0376	0389	0401
4	0414	0427	0439	0451	0463	0475	0486	0498	0510	0522
5	0534	0546	0558	0570	0582	0594	0605	0617	0629	0640
6	0652	0664	0676	0688	0700	0712	0723	0735	0747	0759
7	0770	0782	0794	0805	0817	0829	0840	0851	0862	0874
8	0886	0897	0909	0920	0932	0944	0956	0968	0980	0992
9	1004	1016	1028	1040	1052	1064	1077	1089	1101	1114
10	1126	1136	-	-	-	-	-	-	-	-

Correction for bridge lead resistance.

Cell selector left = -0.058 ohms

Cell selector right = -0.275 ohms

Readings with ratio arms direct were 0.084% higher than those with ratio arms reversed: therefore to correct readings on 0.000049 N solutions (see p. 96), subtract 0.042%.

Corrections for inequality of length of balance arms

B I (Nov. 1950) = -0.0132%
B I (Aug. 1951) = -0.0145%

B II = +0.008%

B III = +0.003%

Calibration of weights

W I

Wt. grams	Corr. mg. (Nov. '50)	Corr. mg. (Aug. '51)
100	-0.6	-0.6
50	-0.4	-0.4
20	0.0	0.0
10	0.00	0.00
10*	0.00	0.00
5	0.00	0.00
2	0.00	0.00
1	+0.03	+0.03
1*	+0.15	+0.15
1**	+0.01	+0.02

Wt. mg.	Corr. mg. (Nov. '50)	Corr. mg. (Aug. '51)
500	+0.095	+0.101
200	+0.012	+0.010
100	+0.023	+0.022
100*	+0.037	+0.041
50	+0.019	+0.022
20	+0.035	+0.030
10	-0.065	-0.063
10*	-0.012	-0.011
5	+0.002	-0.001
2	+0.003	+0.008
2*	0.000	+0.002
1	+0.006	+0.007

W II

Weight grams	Correction mg.
1000	-6
500	-3
200	-2
100	0
100*	-1
50	+1
20	0
10	0
10*	0
5	0
2	0
1	0
1*	0

Weight grams	Correction mg.
0.5	+1
0.2	0
0.1	0
0.1*	0
0.05	0
0.02	0
0.01	0
0.01*	0

W III

All weights in W III were correct to within 0.1 mg.

Cell lead resistances

Cell II = 0.227 ohms
Cell III = 0.034 ohms
Cell IV = 0.03 ohms
Cell V = 0.080 ohms

Cell constants

Cell I = 0.1095 ± 0.0002

Cell V = 0.1751 ± 0.0001

Experiment on conductivity of water (see p. 98)

Conductivity Cell I nanomhos/cm.	Conductivity Cell V nanomhos/cm.	Difference	Mean
88.8	94.5	5.7	
81.9	87.2	5.3	5.5
76.5	82.0	5.5	

Conductivities of KCl solutions

The readings below were taken during the period February to July 1951. They are arranged in chronological order.

Concentration	Method of prep.	Cond. water nanomhos per cm.	Equiv. cond. or cell const. Cell II	Equiv. cond. or cell const. Cell III
0.01 D	Direct	76	0.11850	1.0639
0.01 D	D	85	0.11850	1.0639
0.01 D	D	81	0.11851	1.0638
0.01 D	D	80	-	1.0639
0.01 D	D	71	-	1.0639
0.01 D	D	72	-	1.0639
0.0049 N	D	80	143.63	143.65
"	D	71	143.67	143.67
"	D	69	143.64	143.67
"	D	69	143.67	143.68
0.0049 N	D	74	143.66	143.68
"	D	71	143.66	143.66
"	Indir.	89	143.66	143.65
"	I	75	143.64	143.65
"	I	78	143.67	143.69
0.0049 N	I	78	143.66	-
0.01 D	D	92	0.11850	-
0.01 D	D	89	0.11852	-

Concentration	Method of prep.	Cond. water nanomhos per cm.	Equiv. cond. or cell const. Cell II	Equiv. cond. or cell const. Cell IV
0.01 D	D	85	-	1.0695
"	D	83	0.11850	1.0695
"	D	85	-	1.0696
0.003969 N	D	111	144.22	144.20
"	D	105	144.24	144.21
"	D	94	144.24	144.23
"	D	110	144.23	144.23
0.003969 N	I	96	144.25	144.23
"	I	86	144.25	144.22
"	I	39	144.25	144.23
0.003136 N	I	83	144.85	144.82
"	I	101	144.82	144.78
"	I	82	144.85	144.81
"	I	86	144.82	144.79
0.002401 N	I	94	145.46	145.40
"	I	92	145.45	145.40
"	I	101	145.45	145.40
0.001764 N	I	90	146.09	146.03
"	I	89	146.09	146.03
"	I	88	146.14	146.08
"	I	81	146.11	146.05
0.001225 N	I	83	146.78	146.69
"	I	89	146.74	146.65
"	I	82	146.73	146.66
"	I	76	146.79	146.71
0.000784 N	I	90	147.40	147.29
"	I	98	147.38	147.28
"	I	87	147.39	147.29
0.000441 N	I	103	148.07	147.91
"	I	97	148.07	147.95
"	I	97	148.02	147.86
"	I	92	148.07	147.95

Concentration	Method of prep.	Cond. water nanomhos per cm.	Equiv. cond. or cell const. Cell II	Equiv. cond. or cell const. Cell IV
0.000196 N	I	102	148.84	148.60
"	I	96.3	148.86	148.70
"	I	79.9	148.90	148.70
"	I	80.0	148.89	148.73
0.000049 N	I	82.5	150.07	-
"	I	80.0	149.69	-
"	I	81.4	149.85	-
"	I	81.6	149.82	-
"	I	82.3	149.83	-
0.01 D	D	84	0.11852	1.0696
"	D	90	0.11852	1.0696
"	D	90	0.11853	1.0696

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AN AUTOMATIC RUCYCLING CONDUCTANCE WATER STILL

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OPSOMMING

'n Elektries verhitte distilleerapparaat waarin die water in twee stadia gedistilleer word, eers uit alkaliese permanganaat en dan uit fosforsuur, word beskryf. Toebehore wat 'n konstante waterpeil en veiligheid verseker word gebruik sodat die apparaat lang tydperke sonder aandag kan werk. 'n Outomatiese toestel laat die water sirkuleer as dit nie uit die opvangsfles verwyder word nie; gevolglik word die lang opwarmingsperiode wat noodsaaklik is in die geval van die gewone distilleerapparate, vermy. Daar word ook aangetoon dat die verwydering van ammoniak uit die distilleerketel gevolg deur die verwydering van koolstofdioksied uit die geleiding-sel beter resultate lewer as wanneer albei gassetegelyk uit die distilleerketel verwyder word. Hierdie distilleerapparaat lewer water met 'n geleidings vermoë van minder as 0·09 mikromhos per centimeter; die beste monsters het 'n waarde van 0·071 bereik. Die apparaat verskaf ongeveer 16 liter water per dag.

SUMMARY

An electrically heated still is described in which the water is distilled in two stages, first from alkaline permanganate and then from phosphoric acid. Constant-level and safety devices are employed to enable the still to run for long periods without attention. An automatic device allows the water to be recycled when none is being taken from the still, thus avoiding the long "warm-up" period necessary with conventional stills. It is pointed out that removal of ammonia in the still and of carbon dioxide in the conductance cell gives better results than removal of both gases in the still. When used in this way the water from the still has a conductivity below 0·09 micromhos per centimetre, the best water obtained reaching 0·071. The still will deliver up to 16 litres of such water per day.

The work reported in this paper is part of a research programme originated by Professor W. F. Barker in this laboratory.

In the execution of this programme, recent measurements of the conductances of very dilute aqueous solutions of electrolytes have necessitated the use of water of the lowest conductance attainable in routine work. The literature abounds with descriptions of stills for the production of conductance water; in their original forms several of these are capable of delivering daily several litres of "ultra-pure" water of conductivity better than 100 nm. percm. (1 nmper.cm. =1 nanomho per centimetre $= 10^{-9}$ ohm^{-1}cm^{-1}) at 25° C. In general use, however, these stills do not seem to perform quite as well as this, and the common range of conductivity of the water used in precision conductance research has been from 200 to 600 nm. per cm.

It is commonly found that the water obtained from a still improves in quality from the time of starting the distillation, and reaches its lowest conductivity after several hours; this effect is probably due to the leaching out of those parts of the still which have not been in contact with water for some time. The still described in this paper is arranged to operate automatically for several weeks, the water, once it has filled the collecting vessel, being siphoned back into the reservoir. In this way it is possible to obtain water of excellent quality as it is required, without having to wait for the still to be leached out.

The hydrogen and hydroxyl ions present in water contribute 55 nm. per cm. to its conductivity at 25° C.; it is generally believed that the remainder is due to carbon dioxide in the water. Work carried out in this laboratory has suggested that a large part of the residual conductivity is due to the ammonium and bicarbonate ions formed from the small amounts of ammonia and carbon dioxide in the air. This work, to be published later, also suggests that, while residual carbon dioxide is easily removed from the water by a current of carbon-dioxide-free gas, this procedure does not effectively remove it if ammonia is present. Hence it is desirable to remove all the ammonia before the water is used, a fact which has been stressed by Bjerrum[1] and by Ellis and Kiehl[2] among others.

In the present still a second distillation of the water from phosphoric acid solution is used to accomplish this end. The use of this acid in the preparation of conductance water has been suggested from time to time (e.g., by Bourdillon[3]), but the decision to use it in the present case was taken on the basis of the excellent results obtained by Ellis and Kiehl[2] in their work on the pH of distilled water, and has been fully justified by the performance of the still.

By the technique in which the ammonia is removed in the still and the carbon dioxide is removed later in the cell we have found it possible to use water of conductance 80—90 nm. per cm. as a routine practice. Many stills previously described in the literature as capable of delivering water of conductivity less than 70 nm. per cm. use a counter-current of purified air or condense only a fraction of the steam in order to free the water from gaseous impurities. The water is then used in the conductance cell without further blowing out. Careful study of later papers from those laboratories in which such stills were used, however, has failed to disclose any reports of experimental work in which the conductivity of the water was less than 120 nm. per cm.[4]

Description of the still

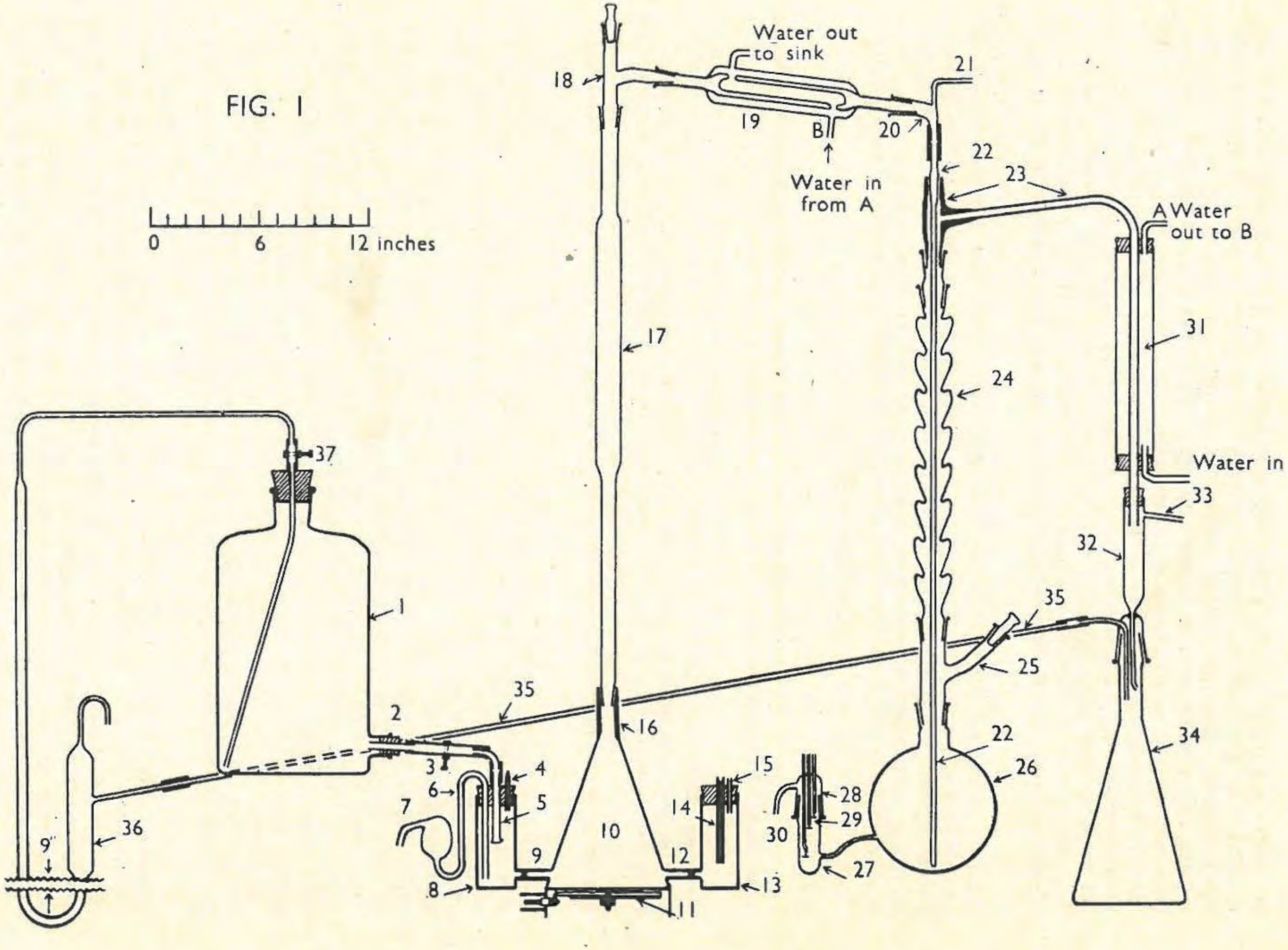
Figure 1 is a diagram of the still. The water for distillation is contained in the 10 litre Pyrex aspirator 1, from which it flows through the constant-level device to the boiler 10. The latter is an 18—8 stainless steel conical vessel with two side cups 8 and 13 of the same material, which are welded to the connecting tubes 9 and 12. These connecting tubes are made of ½-inch stainless steel rod and have for ½ inch of their length holes of diameter 1/32 inch, connecting the ⅜ inch holes from either end; the purpose of the small holes is to permit slow transfer of liquid through the tubes without allowing the level in the cups to change rapidly as the liquid in 10 swishes round when boiling.

The cup 8 carries, through a rubber stopper, the inlet tube 5, the height of which determines the level of liquid in 8, 10 and 13. It also carries the level-indicator tube 6 and the air-leak tube 4 which consists of a short length of capillary tubing drawn to a diameter of about 0·3 mm. The tube 5 is flared at its lower end and has a spout like that of a beaker at one side. When the level in 8 falls below the end of this tube, bubbles of air enter and travel up into 1 by way of the slightly inclined tube 2, allowing water to enter 8 and so hold the liquid level constant. By having the small air leak 4 and the wide portion 7 on the level-indicator, liquid flows back from 7 into 8 during the bubbling process and so limits the amount of water entering to a quantity which can be handled by the cup and connecting tube 9. The overflow on 7 is a safety device in case air should get into 1 by some mishap; it discharges into a sink.

The boiler 10 contains enough sodium hydroxide to make the solution about normal, and enough potassium permanganate to make it about decinormal; the purpose of this mixture is to oxidize organic matter in the water and to hold back acid impurities. Because of the rapid action of the mixture on glass, it is essential to have the boiler made of some resistant material: the 18—8 stainless steel has been found eminently satisfactory for this purpose. The boiler is heated by a 900 watt urn element 11, which is controlled through a safety relay in conjunction with the electrode 14 as described later.

At the top of the boiler is the standard-taper socket 16, turned from stainless steel and welded to the boiler; it is designed to take the B24 joint at the foot of the spray trap and reflux column 17. This is surmounted by the stillhead 18, condenser 19 and adapter 20, all of which have standard-taper joints. The adapter connects with the inlet tube 22

FIG. 1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12 inches
Water out to sink
Water in from A
A Water out to B
Water in
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9"
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to the second boiler 26 by a glass-to-glass joint in pressure tubing, which gives a little flexibility when assembling the still. The lower end of 22 is drawn down to about 1mm. diameter to prevent solution from 26 blowing up and back into 10 if severe bumping should develop. The adapter carries also a tube 21 which is connected to a 2 litre flask (not shown) which communicates with the air. This flask acts as a buffer to prevent excessive "breathing" of laboratory air during boiling. Provision is made for a guard tube on the inlet.

The second boiler 26 is a 2 litre round-bottomed flask with the control device 27 sealed on by way of a length of 0·7 mm. capillary tubing, and is heated by a two-element flask-heating oven of special design. This flask contains approximately 0·1 M. phosphoric acid solution. It is connected by means of a B34 joint to the adapter 25, which carries the pear-bulb fractioning column 24 to act as a spray trap and reflux device, and which also has a side arm through which a porcelain chip may be inserted if bumping commences. Above the fractionating column is the cast block-tin stillhead 23, which has standard half-taper joints to fit the column and to carry the inlet tube 22. The tin take-off pipe from the stillhead is inclined upwards so that the first condensate will return to 26. The steam is finally condensed in the vertical portion 31, from which it falls through the adapter 32 into the 2 litre conical collecting flask 34, which has a B34 cone joint to fit the cap on the adapter as shown. The tube 33 connects with a 1 litre buffer flask which communicates with the air through a guard tube containing soda lime (for CO_2 and HCl), cupric chloride dihydrate (for H_2S), solid metaphosphoric acid (for NH_3) and more soda lime, in that order from the inside.

When the flask 34 has filled, the water is forced through the recycling tube 35 by the head which builds up in 32, and siphons intermittently down the sloping tube into the bulb 36. Since the latter is connected with the reservoir 1 by way of 37, the natural level of the water in 36 is the same as that in 8; thus when returned water runs into 36 it is eventually transferred to 1 to take the place of water leaving through 2, and becomes recycled. Provision is made for a guard tube at the top of 36.

The apparatus is mounted on a framework of three cross-braced retort stands screwed to a wooden base; a wooden stand is provided for the aspirator 1.

The electrical control apparatus

Since the still is required to operate unattended for long periods it is necessary that it should be protected against various kinds of fault which may develop. Also, it will be evident that some means is necessary for ensuring that water distils off from the second boiler 26 at a rate equal to that at which it enters from 10, otherwise 26 will fill and overflow or boil dry and crack. Both these ends are achieved by the use of a simple electrical control system.

The boiler 26 is heated by a specially made hotplate containing two elements, one o 750 watts and one of 600, spirally wound on an alundum base shaped to fit the flask. The 750 watt element is permanently on, but both it and the 900 watt element 11 of the first boiler form the load of a Sunvic type F 102–4 hot-wire relay. The control circuit of this relay is modified so as to connect to the line on one side and to the electrode 30 in the control device 27 on the other side. Electrode 29 is connected to the stainless steel electrode 14 in the control device 13 of the first boiler, and the metal boiler itself is earthed (Figure 2). This ensures that the permanent heaters will only function if the liquid level in 13 is above the end of the electrode 14 and if the level in 26 is sufficiently high to cover electrode 29. If the supply of water from 1 should fail for any reason, or if 26 should crack, this control circuit will at once switch off the heaters. Also, because of the connexion *via* earth and the neutral wire, the still cannot be put into operation if the earth contact on 10 is faulty, nor if the mains plug is inserted the wrong way round.

An automatic recycling conductance water still

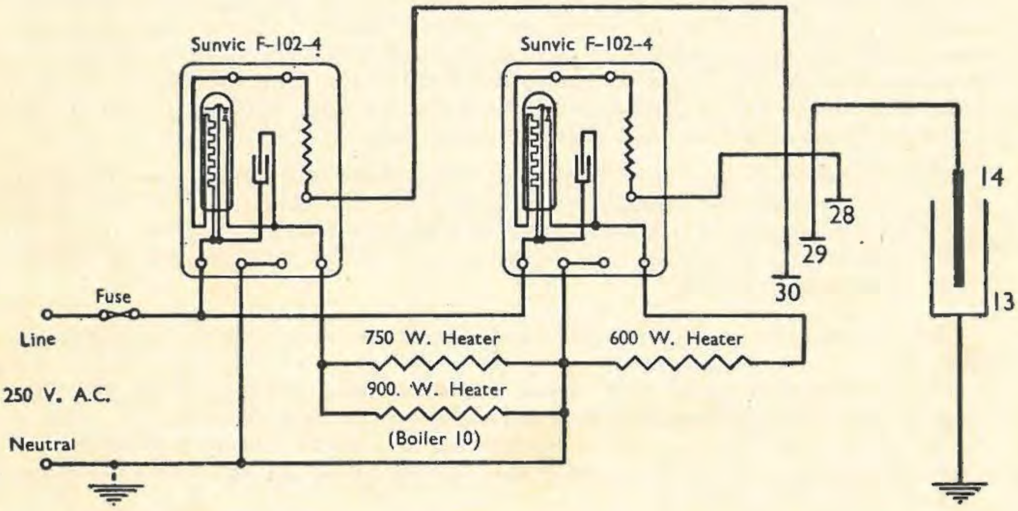

FIG. 2. Electric control circuit

The 600 watt intermittent heater for flask 26 is controlled through a similar Sunvic relay, the control circuit of which operates through electrodes 28, 29 and 14 to earth. Thus when the fast distillation from 10 brings the liquid level in 26 to that of electrode 28, the second heater is energized and, since the total wattage input to 26 now exceeds that to 10, the level falls again until contact with 28 is broken, and flask 26 refills until the cycle starts again.

The electrodes 28, 29 and 30 are horizontal pieces of thick platinum foil of area about $\frac{1}{4}$ square centimetre, with stout leads which are sealed to the mercury-filled Pyrex lead-tubes by Corning 707 glass and uranium glass.[5] The lead-tubes are brought out by internal seals through a cap with a B34 socket, making the electrode assembly easily removable when the still is to be cleaned. Electrode 14 was originally constructed in a similar way, but was found to be attacked by the caustic soda so that the platinum wire became loose and the electrode fell out of the glass tube. It was replaced, therefore, by a stainless steel rod as shown. It is not practicable to have this electrode in cup 8 and thus to eliminate one of the two cups, because when the still recycles, 8 is full of very pure water which does not conduct well enough to close the circuit.

Performance

The still delivers 2 litres of water into the receiving flask in 3 hours, so that 16 litres a day may be obtained from it if desired. Normally it is allowed to recycle overnight, and the convenience of having a flask full of good conductance water first thing in the morning would alone justify the continuous operation principle. Ordinary laboratory distilled water is used to fill the reservoir 1 when necessary. The pinchcocks 3 and 37 are first closed and afterwards opened slowly to prevent overflow of solution from 7. When poured from the flask into the cell in the air of the laboratory the water has a conductivity of about 800 nm. per cm.; after blowing out with carbon-dioxide-free air for about an hour, the time depending on the bubbling rate, the conductivity falls to a minimum which is between 80 and 90 nm. per cm. The best sample measured had a conductivity of 71 nm. per cm. This may be compared with the value of 62 nm. per cm. (recalculated to 25° C.) reached by Kohlrausch and Heydweiller in their classical experiment which involved 42 distillations *in vacuo*,[6] and with the figure of 66 nm. per cm. for the best water obtained by Kraus and Dexter from their still.[7]

When the water is kept in well-seasoned Pyrex flasks with tinfoil-covered rubber stoppers its conductivity increases by less than 1 nm. per cm. per day at 24° C. In a cell where it is agitated by bubbling the rate of increase is somewhat higher.

The chemicals in the boilers need replacing every month, or whenever the quality of the water starts to fall off.

Work on the early forms of the still was done in conjunction with Mr. G. N. Festenstein, MSc.

We are indebted to Mr. G. McP. Malan, BSc. for criticism and suggestions, and for a large number of measurements of the conductivities of samples of water.

One of us (A.F.) held a research studentship awarded by African Explosives and Chemical Industries during the period of development of the still, and wishes to express his gratitude to that company.

Note added in proof: Since submitting this paper the figure of 71 nm. per cm. for the best water has been improved upon by using purified nitrogen instead of air for the stirring gas. The best water obtained in this way reached 62 nm. per cm.

To guard against failure of the town water supply to the condensers a perforated bucket on a pivoted arm carrying a mercury switch has been inserted between electrodes 29 and 14, and the outflow water from the condensers passes through this bucket. This device has proved its worth on several occasions.

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