THE CONSTRUCTION OF A PRECISION CONDUCTANCE BRIDGE AND ITS APPLICATION TO A STUDY OF CHROMIUM SULPHATE COMPLEXES.

A Thesis Submitted in Part-fulfilment of the Requirements of the University of South Africa for the degree of M.Sc.

By

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PART I.

CONSTRUCTION OF THE CONDUCTANCE BRIDGE.

A. INTRODUCTION.

The principles underlying the construction of precision conductance bridges have been established by the pioneer work of Jones and Josephs (1) and by Shedlovsky(2). Recent developments in radio engineering have made possible several improvements in bridge assemblies without, however, increasing greatly the precision of the measurements. That obtained by the above workers is still sufficient for most purposes.

A bridge incorporating these principles was built in this department by Gledhill (3) in 1941. He observed all the precautions mentioned by the above workers except where experiment had shown them to be unnecessary. The bridge is housed in a specially constructed constant temperature room, and has proved to be very satisfactory in operation.

In the new design, more attention has been paid to increasing the ease of manipulation of the bridge, rather than to increasing its precision. It was planned to use a cathode ray oscilloscope as detector, and to consider the possibilities of new designs for the oscillator and amplifier units.

B. THE CONSTANT TEMPERATURE ROOM.

REASONS FOR BUILDING THE ROOM.

Almost all conductance measurements are made at 25°C. In summer the temperature of the atmosphere often rises to 30°C., and even in a cool room it will rise to 25°C. To maintain a thermostat at 25°C, under these conditions, some form of cooling is essential. The most obvious method is the addition of ice to the thermostat; this, however, would make accurate temperature control very difficult, and is, in any case, most inconvenient. The most satisfactory method is to cool the air in the room in which the measurements are being taken, and the temperature of the thermostat may then be controlled by a simple "on-off" relay. In order to cool the air in the room, it is essential to insulate the walls of the room.

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

(i) It is much easier to control the temperature of a thermostat if it is in a room in which the temperature is sensibly constant, and not much lower than the value to which the thermostat is set.

(ii) In carrying out a conductometric titration, if the temperature of the small amounts of solution added to the cell differs widely from the temperature of the thermostat, a pause must be made after each addition, to allow the contents of the cell to reach temperature equilibrium with the thermostat. This is not necessary if the difference in temperature is small, i.e. if the room temperature is adjusted to remain at a value slightly below the thermostat temperature.

(Note: If a weight burette is to be used for making additions to the cell (as is necessary in accurate work), it is desirable to have a balance in the room, for the above reason).

(iii) A constant temperature room (referred to in future as c-t room) is useful for many physical measurements, which require constant temperature for operation, where high precision of temperature control is not necessary.

For these reasons, the aim was to build a room in which the temperature could be maintained constant at 24°C., to within 0.1°C.

A room, conforming to these requirements, had been built by Gledhill and Thomas in 1941. The walls of the room are insulated with sawdust. Fresh air is brought into the room by means of a fan mounted in one wall, and the temperature of the room controlled by regulating the temperature of the incoming air. This system is very satisfactory and has been adopted in the new c-t room.

The task of drawing up a design was greatly facilitated by the experience of Gledhill and Thomas in their work, and also by the suggestions of Messrs Faure and Festenstein, who later worked in the room.

Choice of Site.

The first point to be considered was the choice of a suitable "outer room". The choice was governed by two factors :

(i) The room had to be sufficiently large to contain the c-t room (an obvious point).

(ii) The temperature of the room had to vary as little as possible. More particularly, in summer the room had to remain relatively cool.

Of the rooms available in the Chemistry Department, that conforming most nearly to these requirements was, at the time of choice, the Department workshop. With regard to factor (i), it is satisfactory being 19½' long, 13' wide and 13½' high; with regard to factor (ii), it is well insulated from the outside by thick brick walls. On the East side, it has a window which is protected from the sun's rays, except for a short period in the early morning, by a covered sidewalk. The room does not become very hot in the day-time nor unduly cold at night, and over a period of 24 hours, its temperature does not fluctuate much.

Regular readings of the temperature were taken during the months of December and February; at no time did it rise above 25°C. It would have been difficult to find a room cooler than this during the summer.

Construction of the Constant Temperature Room.

The plan is shown in Fig. I. The room is 11' 6" long, 9' 4" wide, and 6' 5" high. It is enclosed on the South, West, and East sides, and on the top, by the walls and ceiling of the "outer room". The floor is 6' 4" above that of the latter, the intervening space being used for storage (not for general use as, in summer, it is inadvisable to have any major source of heat e.g. gas burners, human beings, in this space). The North wall is 7' from the corresponding wall of the "outer room", part of the intervening space being occupied by stairs to the room.

The framework of the floor is of wooden beams, 6" thick and 1½" wide, the distance between adjacent beams being 2'. These are covered on the top with wooden flooring boards, and on the bottom with celotex. The empty space in the frame work is filled with sawdust to cut down heat transfer. The walls and ceiling are made of a similar framework, the beams being 3" and 4" thick, respectively. This framework is covered on the inside with celotex (in the case of the North wall, on the outside as well), and

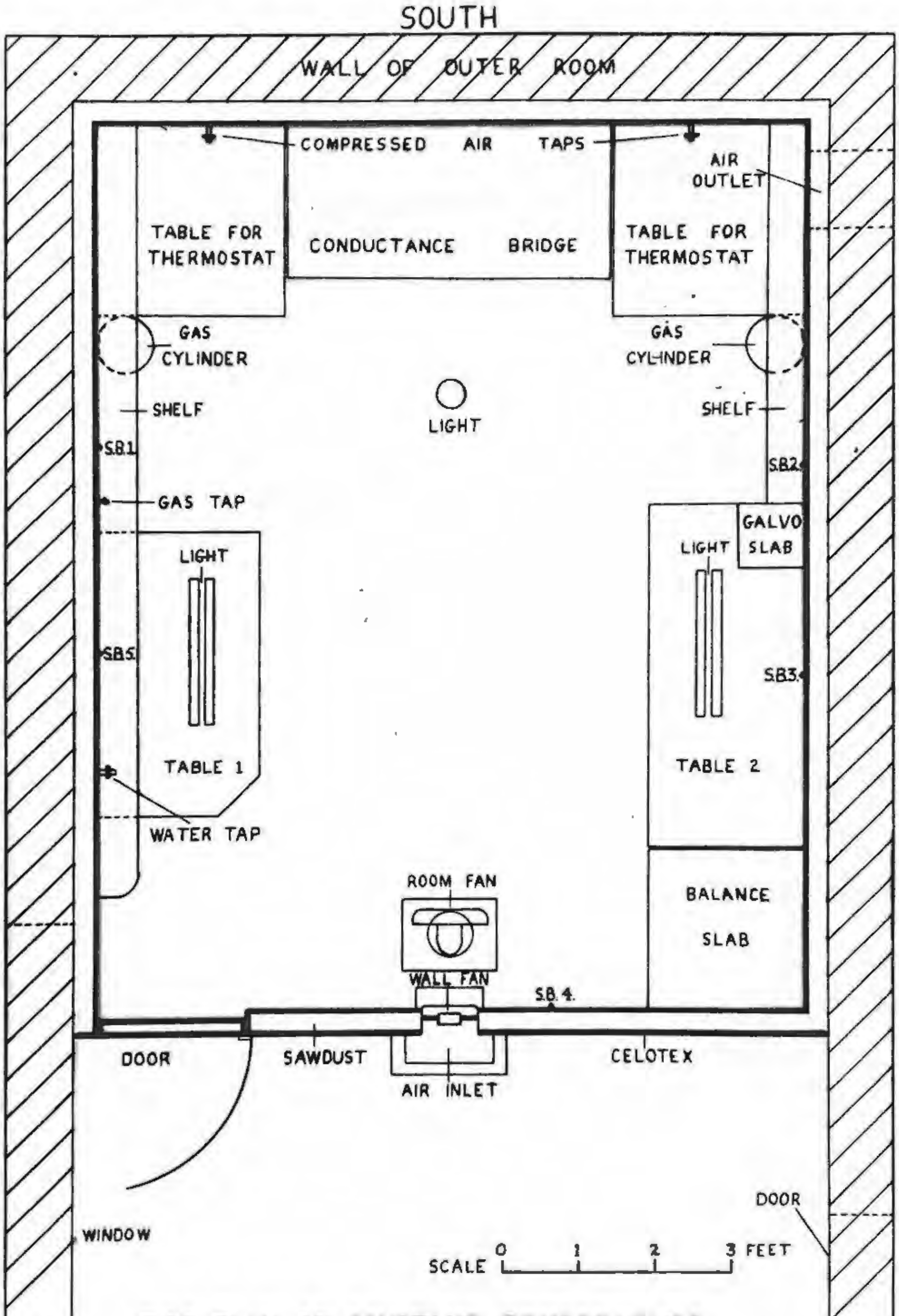

FIG.I. PLAN OF CONSTANT-TEMPERATURE ROOM the intervening spaces again filled with sawdust. The door of the room is built on a framework 1½" thick, 23½" wide, and 6' 4" high, and is covered and packed in the same way as the walls. A spring keeps it in a closed position. The door is situated in the North wall, and it opens onto a landing with a flight of 8 steps rising from a point 2½' from the West wall of the "outer room".

The air inlet is a circular hole, in the North wall, of 9" diameter, 4' 6" above the floor. The air outlet is a rectangular opening, 12" x 10½", in the South corner of the West wall, and 5' above the floor; it may be closed by means of a trap door.

Internal Arrangement.

It was apparent that the internal arrangement of the Gledhill-Thomas c-t room is not the most convenient one. The main defect is that the bridge and thermostats are cramped into a small section of the room, and, in general, the available space is not used to best advantage. It was therefore decided to use the whole of the South wall to accommodate the bridge and the two thermostats (see Plate II); as a result, the dimensions of the bridge were increased, and hence its convenience in operation (see later).

The thermostat tables are 2' 6" square, 16" high, and are situated in the two corners; the bridge fills the space between them. In the room, there are two tables for general use : table 1 (East wall) is 2' 2" wide, 3' 9" long and 2' 8" high; table 2 (West wall) is 2' wide, 4' 7" long and 3' high. A carefully levelled, slate slab (24" x 19" x 1½") was cemented into the North end of the West brick wall, at a height of 3' above the floor. It is held rigidly in position by two iron angle brackets. In addition, a carefully levelled slab (10" x 10½" x 1½") was let into the West brick wall, 5' above the floor. It is held in position by contilever action, and supports a galvanometer, which is used in electrochemical experiments.

For the disposal of apparatus, there are two shelves (6" wide) on the East and West walls, at a height of 4½' above the floor. Below these, there are two smaller shelves, 6" wide, 23" long and at the same height as the thermostat tables. There is a gap of 9" between each thermostat table and the corresponding lower shelf. Thus, if it is necessary to stir the contents of the cell with some gas other than air (4), a cylinder may be placed in this gap, and held in a vertical position against the wall. This arrangement obviates the considerable inconvenience of having bulky cylinders lying on the floor.

Cold water, gas and compressed air are supplied at the points shown in Fig. I.

Room lighting.

In building a c-t room, it is desirable to keep internal sources of heat at a minimum. The room is illuminated by two twin 20 watt lamps of the fluorescent mercury vapour type, one above each general purpose table. This is the most efficient source of light in common use, and, although only 80 watts are dissipated, the room is very well lit. This type of lamp has the disadvantage of taking several seconds to "strike". For convenience, therefore, a lamp of the ordinary filament has been installed above the bridge; it is of the "daylight" type, to harmonise with the mercury vapour lamps, and is fitted with a 3-way switch. It is used only when the room is occupied for a brief period; when work is carried out in the room for any length of time, it is not used, as the other lights are sufficiently bright, and the former one only provides an extra source of heat.

Power to the Room.

A.C. is supplied to the room on five switchboards, as shown in Fig. I. The power to these is controlled by a switchboard mounted beneath the c-t room, and this also controls the power to the refrigerator. It was decided to standardise on one type of plug, except in some special cases cited later. That chosen was the 15 amp - 3 prong type, and, unless otherwise stated, the term "plug" will refer to one of these. The switchboards are wired so that the left hand pin is neutral, the right hand pin line, and the third pin earthed separately (except in the case of the special heater circuit on switchboard 4).

Switchboard 1 consists of five plugs, each with its own switch and fuse. It supplies power to the oscilloscope, and to the heater, relay, and stirring motor of thermostat I. There are two spare plugs.

Switchboard 2 has 4 plugs each with switch and fuse. It supplies power to the oscillator, and to the heater, relay, and stirring-motor of thermostat II.

Switchboard 3 has 4 plugs, each with switch and fuse. The third switch and fuse supply power to a 10 amp 2 pin plug, a 5 amp 2 pin plug and a bayonet socket. The board is for general purpose.

Switchboard 4 is divided into two sections, (a) and (b). (a) has a switch and fuse controlling power to the whole board. Below this is a plug, the right hand pin of which is connected permanently to line, and supplies power to the room relay. The third pin is connected, through a fuse, to a three heat switch, which controls the power to the room heater (the wiring of the three heat switch being conventional). The room relay closes between the right hand pin and the third pin; the left hand pin is permanently connected to neutral. Below this plug are a switch and fuse controlling power to the "permanent" room heater (see later).

Switchboard (b) has a switch and fuse controlling power to the wall fan. It also has two plugs, each with switch and fuse; one supplies power to the room fan, and the other is for general use. A line runs from the board to a switch and bayonet socket, situated behind the balance.

Switchboard 5 has two plugs, each with fuse and switch, for general use; there is also a permanently live bayonet socket, which energises the room clock.

Provision has been made on switchboards 3 and 5 for D.C., which is obtained from a board in the "outer room". Switchboards 3 and 4 are visible in Plate 1.

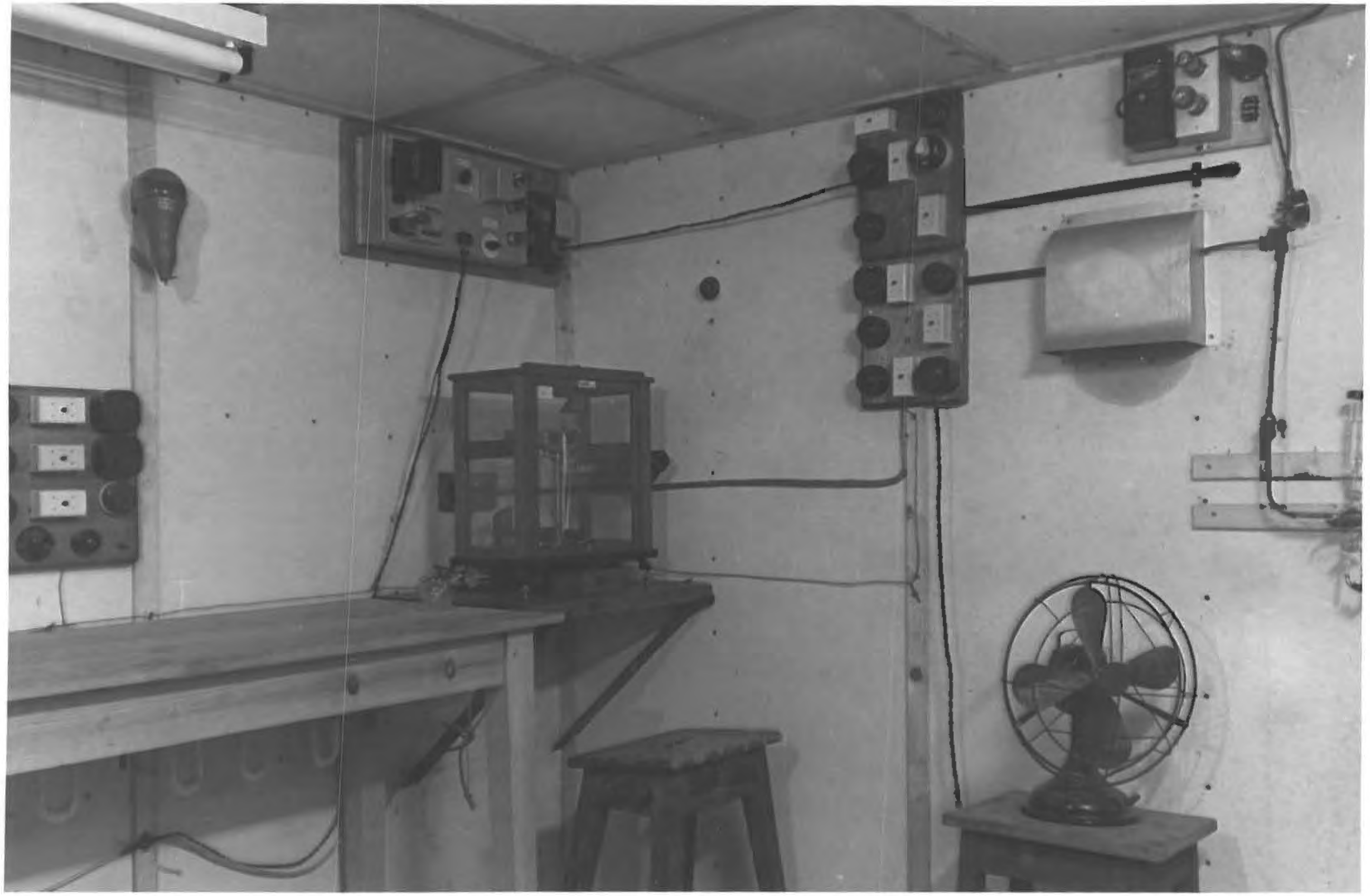

PLATE I

C. CONTROL OF ROOM TEMPERATURE.

The 9" diameter fan in the North wall supplies air to the room; the air is drawn through a duct containing heating and cooling coils, passing first over the latter. The room temperature is regulated by switching the current through the heater on and off. The cooling coils operate continuously when the temperature of the outside air is above 19°C; if it is below 19°C, no cooling is necessary.

The Cooling Plant.

This consists of a 2 H.P.-3 Phase Delco motor, which drives a twin cylinder Mills compressor. The unit is mounted in the basement, in a position most convenient to cool the coils of both new and old c-t rooms. The control switch for the motor is on the switchboard beneath the new room. When the temperature of the air outside either c-t room reaches a preselected temperature (19°C), a Siebert-Kuhn thermo-regulator operates a relay placed in series with the pressure-operated cut-out of the compressor unit. When the relay opens the circuit, the motor will not run at all; when the relay closes, the motor will run until the pressure cut-out operates. Control is thus fully automatic. For convenience, a switch, in parallel with the thermo-regulator, has been placed in the room near switchboard 4 (see plate I);

this enables the refrigerator to be run at any time, independent of temperature.

(Note: The relay is a Struthers-Dunn, type 29XAX, operated by a 6-volt battery. It runs off a negligibly small current (2 m-amps), and hence the battery need only be replaced about once a month).

The Room Heater.

The main heater coils consist of two 1000 watt oven elements, connected to a three-heat switch, power to which is controlled by the room relay. The power dissipated by these two coils 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 heater coils are wound on grooved porcelain strips, which are mounted on each side of the air duct. The winding of these coils is such that the incoming air is uniformly heated.

Circulation of Air.

The air inlet (containing the wall fan) is covered with a baffle, made of galvanised iron, which deflects the air downwards onto a 12" oscillating fan (see plate I). This directs the incoming air to all points of the room, and the air leaves the room via the outlet in the West wall (see plate X).

Choice of Relay.

The Struthers-Dunn relays used by Gledhill are soundly constructed and efficient; however, they suffer from two disadvantages

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

(ii) they are noisy in operation.

It was decided not to use these, as a superior relay viz., the Sunvic type F102-4, had become available. A circuit diagram of the relay is given in Fig. VB. In this type of relay, contact is made and broken in a high vacuum, so eliminating all sparking, and allowing very light contacts to be used. The contacting device is controlled by the current in a coil of thin wire; when this current (±25 m-amps) passes through the coil, the latter heats up and expands, allowing contact to be made. When the current is decreased, the coil cools down and contracts; the contact is then broken. As there is a time lag (about 2 seconds) between the flow of control current and the operation of the relay, there is little likelihood of "chatter". Also, as the contacting device is in vacuo, the relay operates noiselessly. This type of relay is in use for both room and thermostat temperature control.

Choice of Room Regulator.

The first regulator to be tested was similar to the one described by Gledhill (loc. cit.). It consists of a 30' length of ¼" copper tubing (the main tube), which is run around the room, partly along the ceiling and partly along the walls; there is also a section of tube (the auxiliary tube), of length about 1', in the air stream. The tube is filled with paraffin, one end being sealed, and the other joined onto the contacting device. The latter is similar in construction to the one used by Gledhill. A long time was spent in attempting to operate the regulator satisfactorily, but with only partial success. The three main reasons for this are listed below:

a) it is a matter of some difficulty to exclude air completely, when filling the tubes. This is essential, as otherwise the barometric pressure will affect the room temperature.

b) there was a steady rise in room temperature over a long period of time, and this could only be ascribed to a leak in the regulator. All the tube unions and seals were tightened and sealed with pitch, but this did not check the fault. The only other possible source was in the taps of the contacting device. Although these had been meticulously ground, there appeared to be a tendency for the taps to loosen in their barrels, and this was almost completely overcome by holding the taps in place with rubber bands.

c) the greatest trouble was due to the fact that, when a person entered the room, the temperature rose 0.2°C. The cause of this is known: When a person enters the room, the mean temperature of the incoming air falls somewhat. Accordingly, the paraffin in the auxiliary tube contracts, and the paraffin in the main tube is heated and expands, until the total volume of paraffin is the same as before. This heat could be obtained in two ways:

i) a rise in room temperature

ii) radiation of heat from the person in the room.

In the ideal case, the heat radiated by the person causes sufficient expansion, and the temperature of the room does not alter. This condition is nearly fulfilled in the Gledhill c-t room, where the temperature rises for a brief period, and then falls as soon as sufficient radiant heat has been absorbed. As stated before, in the present room, the temperature rose by 0.2°C. This defect could probably be remedied empirically (e.g. by painting the tube suitably), but would obviously be a lengthy process.

(Note: Gledhill has mentioned that control of temperature, without the tube in the air stream, is unsatisfactory because of the insensitivity of the large mass of paraffin to rapid changes in 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 foul after a few months, in spite of the use of a thermionic relay. This necessitates dismantling and refilling the regulator, which is a very troublesome task.

At this stage, a search through the literature disclosed the fact that there is another method of temperature control, depending on a totally different principle, viz., the variation of resistence with temperature. By using an electronic circuit, this effect can be used to control a heating current, as described below. A relay has been built on this principle, but the regulator described above has been left in position, to act as standby.

The Room Relay.

To understand the principle of operation of the relay, a knowledge of the characteristics of the thyratron is essential. 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 ionising collisions of electrons with molecules is very high, and many ions are consequently present in the gas. The characteristics of such a tube differ~~s~~ markedly from those of the normal triode (See, e.g., Reich (5)).

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 to a value just below the ionising potential of the gas in the tube.

The result is a trigger device, which has numerous practical uses. It takes practically no energy at the grid to initiate the discharge; to stop it, some other form of control is required.

A.C. Operation of Thyratrons (See Fig. II).

If A.C. is applied to the plate of a thyratron

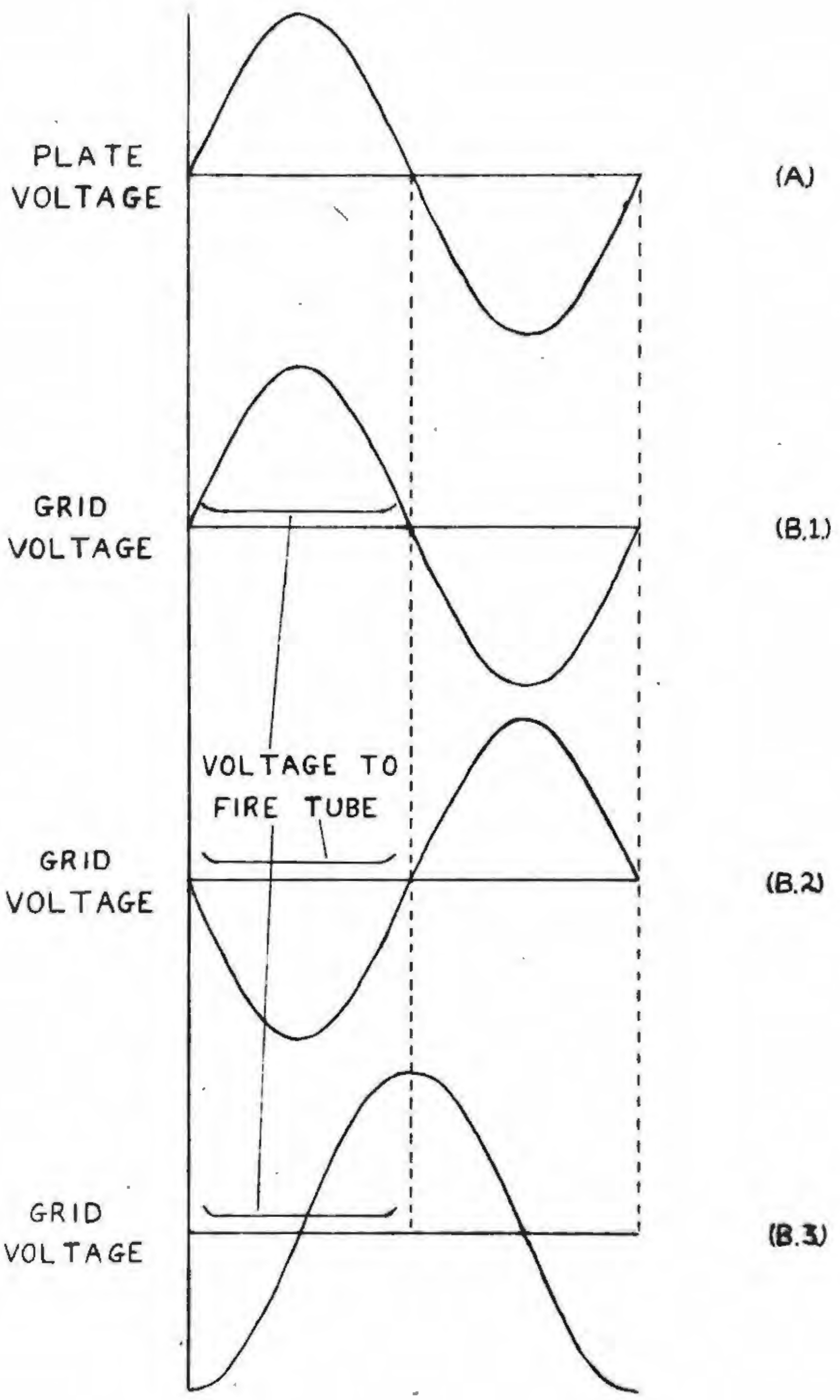

FIG.II OPERATION OF THYRATRON

which requires a small positive grid bias to initiate the discharge, and a small A.C. voltage, in phase with that on the plate, is applied to the grid, the tube will conduct on the positive half-cycle (Fig. (B.1.)). If, however, the grid voltage is 180° out of phase with the plate voltage, the tube will not conduct at all. (Fig. (B.2)). Any mean current between these two limits can be obtained by adjusting the phase of the voltage applied to the grid, e.g., if the voltage is 90° out of phase, the tube will conduct for approximately $\frac{1}{4}$ cycle (Fig. (B 3)).

Control of Temperature with an A.C. operated Thyratron.

If A.C. is applied to a Wheatstone Bridge, one resistance of which varies with temperature, then, as the temperature is increased, the output voltage of the bridge will undergo 180° phase change when the bridge passes through balance. If this voltage is amplified, and applied to the grid of the thyratron, the phase can be so arranged that the tube will conduct when the temperature is below the "balance temperature", but will not conduct above this temperature. The thyratron current can be used to operate a relay of the Sunvic type, placed in the plate load; this, in fact, is the principle of the relay in use.

The design was adapted from a more complex circuit, described by Sturtevant (8). In his circuit, a larger thyratron is used, the current from which is passed through a thermostat heater. 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 out of balance, the phase difference will be slightly less or greater than 90°, according to the phase and magnitude of the grid voltage. The power supplied to the thermostat heater varies accordingly, the bridge being connected so that when the temperature falls, more power is delivered. This type of control is superior to the "on-off" control of the normal regulator : An equilibrium temperature is soon reached, in the case of the former, instead of oscillation about a mean temperature, in the case of the latter. The method is not suitable for use in heating the c-t room, as a very large tube would be required to pass the current which flows in the room heaters.

Construction of the temperature controlling Wheatstone Bridge.

The resistances used in this bridge have to be of good quality: They must remain absolutely constant over a long period of time. A change of 0.04% in any one will change the room temperature by as much as 0.1°C.

A material suitable for the <u>temperature sensitive resistance</u> (R_t) is one which has a high temperature coefficient of resistance; unfortunately, this is a property belonging to the good conductors (e.g. copper, silver). There is, however, an alloy of Nickel and Iron, known as "Hytemco", which has a coefficient of 4×10^{-3} per degree (equal to that of copper), but, unfortunately, none of this was available. Copper wire was eventually chosen, as it is readily obtainable in the form of thin insulated wire.

Sturtevant (loc. cit.) 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. It is impractical to use wire with a resistance of more than ½ ohm per foot, as it would be too delicate to handle. A resistance of 200 ohms, made of ½ ohm-per-foot wire, requires a length of 400 ft, and the task of winding this into a resistance is complicated by the fact that it must be non-inductive; this can be done in several ways (See Hague (7)). The simplest is the bifilar winding. As the resistor has to be at the average temperature of the room (rather than at the particular temperature of any one point), it was necessary to wind the wire on a flexible former, which could circle the room. The material chosen for the former was a good quality rope of ½" diameter and length 35'. The difficulty of making a bifilar winding of thin copper wire, 400' in length, on such a former, is apparent; it was, however, accomplished.

The copper wire was doubled, and the twin thread wound onto the rope, with a space of approximately $\frac{1}{16}$" between adjacent strands. It is evident that, in this type of winding, a short circuit between adjoining threads can short out an appreciable part of the resistance. For this reason, it was decided not to rely on the insulation of the wire, and great care was taken that no threads were contiguous. In addition, upon completion, the resistance was coated with shellac to ensure that the threads would remain in place.

A thin copper wire responds almost instantaneously to changes in air temperature: therefore it was not desirable to place any part of it in the air stream (as was the case with the tube of the paraffin regulator). As no part is in the air stream, it is essential that the resistance should not be heated by

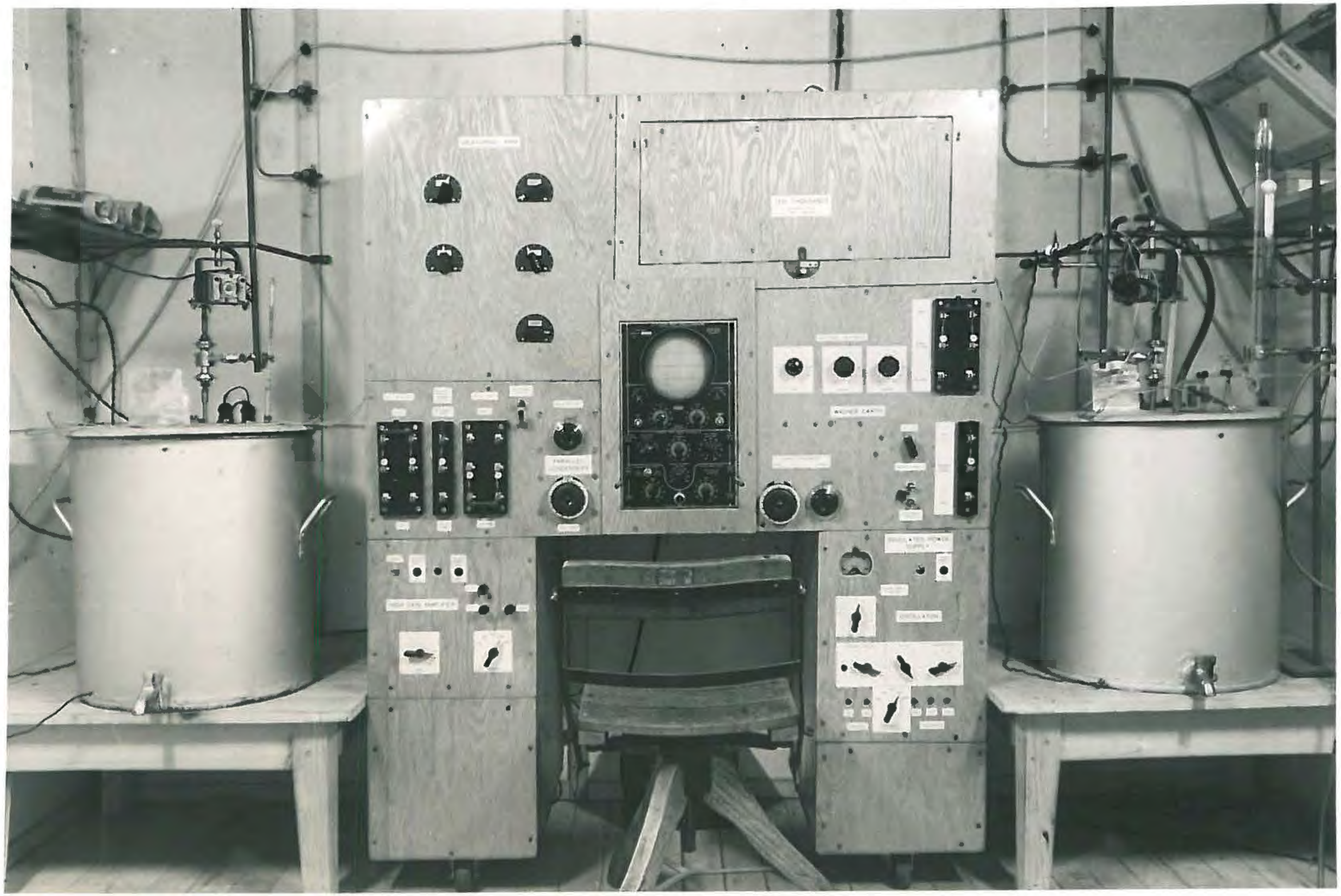
PARALLEL CONDENSERS
WAGNER EARTH
HIGH GAIN AMPLIFIER
REGULATED POWER SUPPLY
OSCILLATOR

PLATE II

radiation. For this reason, it was painted with a reflecting layer of Aluminium paint. The resistance was run along the walls in a position where it is subjected to a minimum amount of radiant heat. (The section along the South wall may be discerned above the bridge in Plate II). No attempt was made to adjust the resistance of Rt accurately to 200 ohms; it was deemed preferable to wind three resistances of the bridge to approximately 200 ohms, and adjust the fourth to the value calculated for balance.

The remaining three bridge resistors are made of manganin wire, which has practically zero temperature coefficient of resistance. The guage used has a resistance of approximately 13 ohms per foot, and about 15 ft. were required for 200 ohms. Each resistor is wound non-inductively on an ebonite strip, the edges of which are grooved to keep the wire in position. To protect the resistances from humidity, they were coated with paraffin wax.

The Thyratron Relay.

The thyratron available, a 6Q 5G, does not require a positive bias on the grid to initiate the discharge. On the contrary, with 250 V. applied to the plate, it requires a high negative bias (30V.) to prevent the discharge. This means that, at the equilibrium

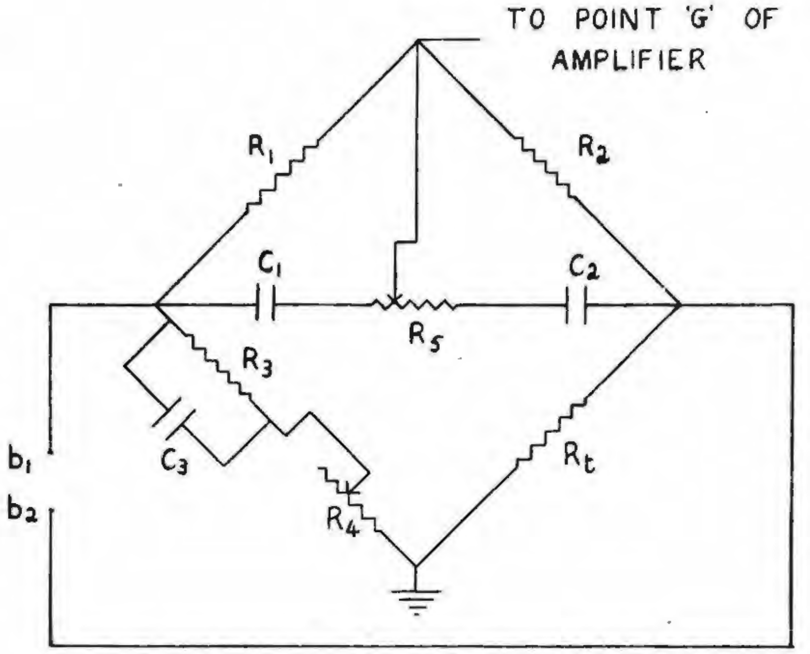

FIG.III(A) RELAY BRIDGE CIRCUIT

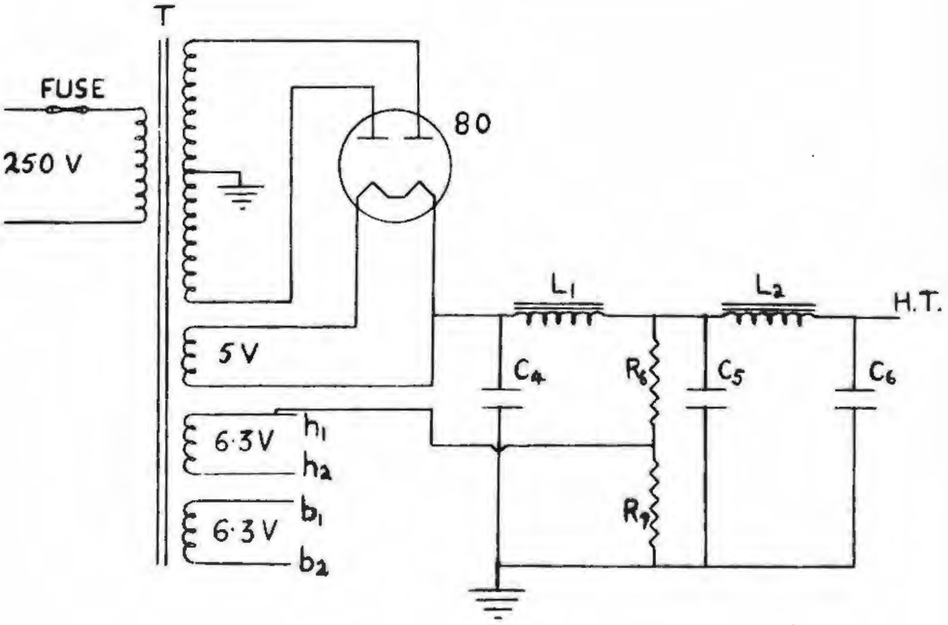

FIG.III(B) RELAY POWER SUPPLY

FIG. IIIA. RELAY BRIDGE CIRCUIT.

R_1 = 187 ohms;
R_2 = 189 ohms;
R_3 = 201 ~~[illegible]~~ ohms;
R_4 = 5 ohms;
R_5 = 100 K ohms.

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 ohms;
R_7 = 10 K ohms;
L_1 = 30 henries
L_2 = 30 henries

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

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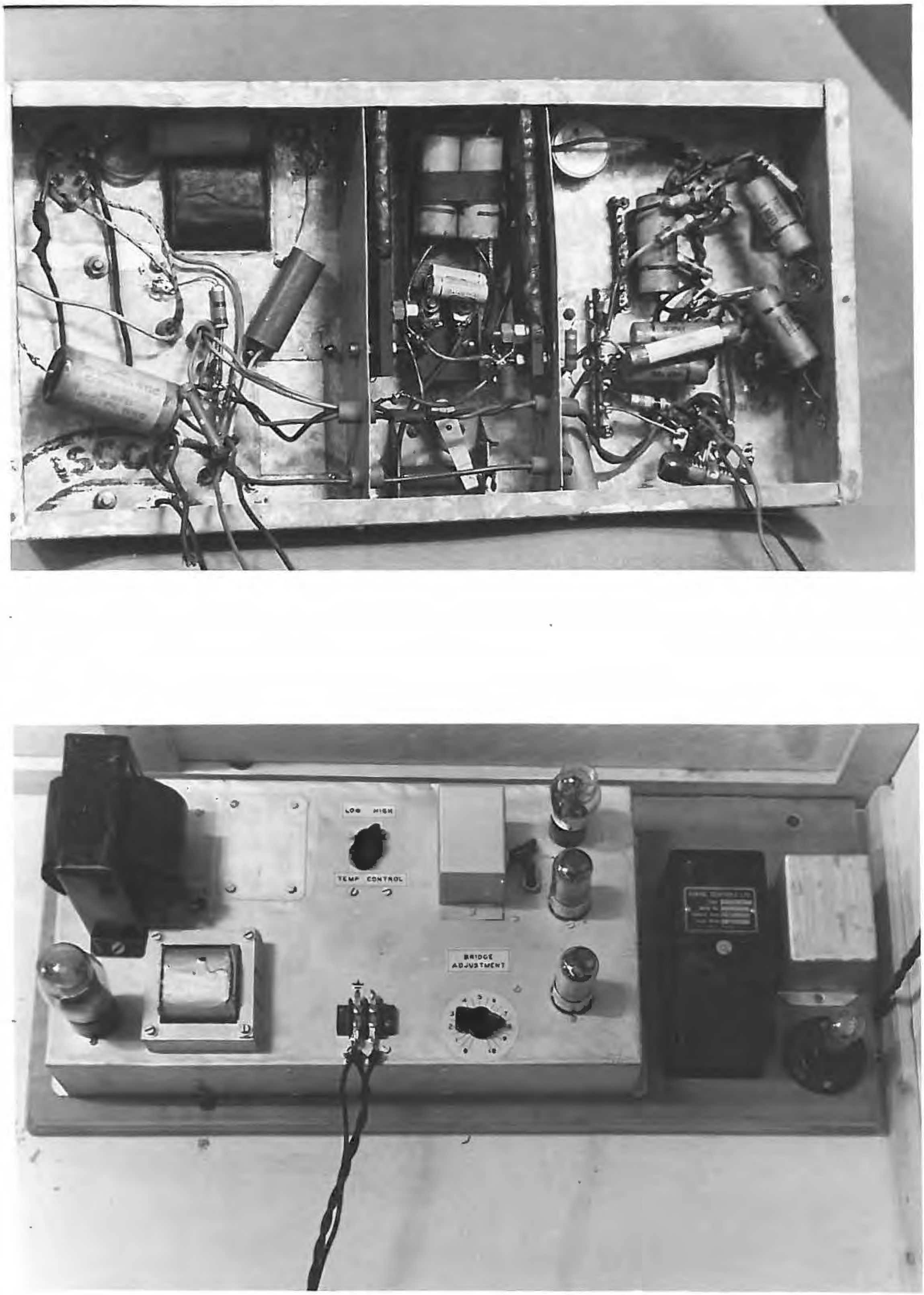

PLATE III

temperature, the bridge will, not be balanced but will be just sufficiently off balance to provide the grid bias necessary to prevent the discharge. Apart from this, the simple theory is complicated by 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. For these reasons, with a simple bridge circuit, the control is not sharply "on-off". A theoretical analysis is impractical; it was essential to obtain the necessary sharpness by empirical methods. The circuit finally chosen has proved satisfactory.

The Wheatstone Bridge (See Fig. III A and Plate III).

The bridge components are situated in the section of the chassis between the power pack and the amplifier, and are shielded from either by galvanised iron. This is the most suitable position for the bridge, as it enables the amplifier to be at a maximum distance from the A.C. transformer used in the power pack. To enable the room temperature to be varied, a low resistance potentiometer, R4 (5 ohms maximum), is placed in series with R_3. Condenser C_3 is included to balance out the stray capacity to earth in the windings of Rt and the transformer. Its value may be found by using a variable condenser, and adjusting the bridge to balance. C_1, C_2, and R_5 are designed to give a component 90° out of phase with the bridge voltage, allowing continuous control to be achieved. In the Sturtevant circuit it is set to maximum sensitivity; if set too far, it gives "on-off" control, as is used in the present room.

Power Pack (See Fig. III B and Plate III)

To achieve the best "on-off" control, A.C., should be kept at a minimum. For this reason, the power pack (which is conventional) is fitted with an extra stage of smoothing. In the original chassis, both L_1 and L_2 were mounted near the mains transformer. However, it was found that there was a certain amount of mutual inductance, which introduced a small A.C. component into the H.T. 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 H.T. supply when it was used to replace batteries in a high gain amplifier. A.C. pickup from the valve heaters may be minimised by giving them a small positive bias with respect to the cathode. This is done by means of the potentiometer arrangement R_6 R_7, the positive bias being approximately 10 volts.

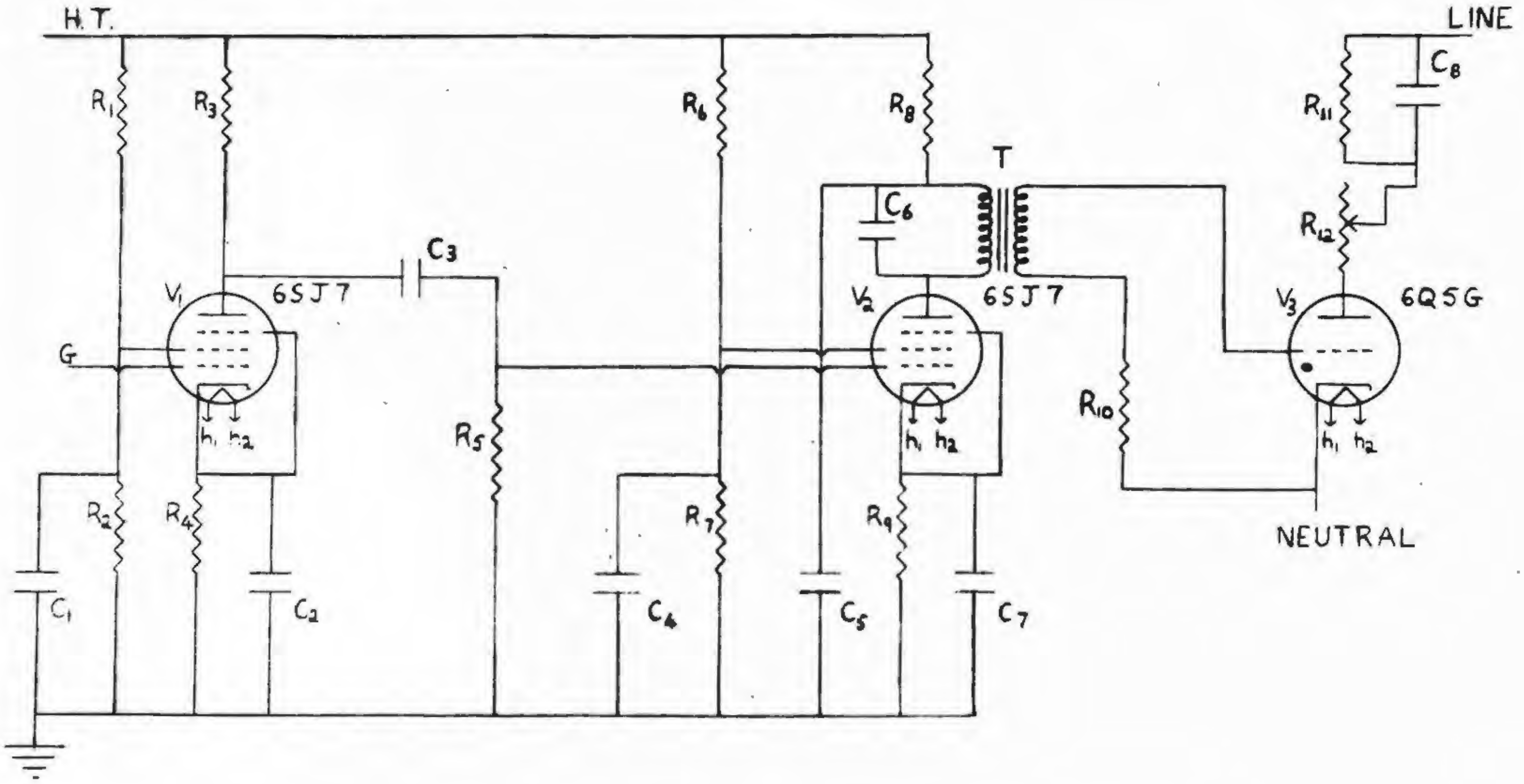

FIG IV RELAY AMPLIFIER AND THYRATRON

FIG. IV. RELAY AMPLIFIER AND THYRATRON.

R_1 = 100K ohms;
R_2 = 50K ohms;
R_3 = 100K ohms;
R_4 = 1000 ohms;
R_5 = 1 M ohms;
R_6 = 75K ohms;
R_7 = 50K ohms;
R_8 = 25K ohms;
R_9 = 500 ohms;
R10= 100K ohms;
R_{11}= relay heater;
R_{12}= 10K ohms, 10 watts.

C_1 = 0·1 μF;
C_2 = 50 μF;
C_3 = 0·25μF;
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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Amplifier and Thyratron. (See Fig. IV and Plate III).

V_1 and V_2 form a two stage amplifier with an overall gain of 10,000. The screen grid voltage is approximately 100, and is obtained by the potentiometer arrangements R_1 R_2 and R_6 R_7, as simple voltage dropping resistors are not recommended when the H.T. is above 300 volts (8). The cathode resistors were chosen to give a grid bias of between 2 and 2½ volts for V_1, and 1 and 1½ volts for V_2. The 50 μF bypass condensers, C_2 and C_7, were installed because they happened to be available; such high values are not strictly necessary. The most obvious type of coupling to use between the output of the amplifier and the thyratron is normal resistance capacity coupling, and this was installed first. It was finally abandoned because the relay would not go off sharply, but tended to "chatter" 10 to 20 times before finally operating. The precise theory is not known - a tentative explanation is proferred: it has been observed that, when the room heater comes on, the line voltage falls by 5; conversely, when the heater goes off, the line voltage rises by 5. Consequently, when the heater goes off, there is a rise in H.T. This gives a positive "kick" to the grid of V_2, which is amplified to give a much larger negative "kick" to the grid of V_3. As V_3 is a gas filled tube, positive ions will be present, and therefore grid current will flow until the coupling condenser has a positive charge which balances out the negative "kick"; when the latter has passed, there will be a resultant positive bias on the grid of V_3, which will fire it again. The relay will go on and off until the bridge is so far off balance, that the coupling condenser is no longer able to fire the thyratron.

This effect can be eliminated by using transformer coupling; with this, the charging of a coupling condenser falls away and the *negative* "kick" at the grid of V_3 reduces the likelihood of the thyratron's firing considerably. The primary of the transformer is tuned to 50 cycles, partly to prevent undesired phase changes, and partly to obtain a plate load of desired magnitude. As there is no D.C. voltage drop, a voltage dropping resistor R_8, with decoupling condenser C_5, is essential. R_{10} is included to limit the grid current of the thyratron. A persistent tendency of the relay to "chatter" was finally eliminated by placing a large electrolytic condenser, C_6, across the heater of the Sunvic relay. R_{12} is included to enable the control current of the relay to be adjusted to a suitable value.

In spite of all the foregoing precautions, absolute "on-off" control was not obtained; the nearest approach was a very rapid change of current in the vicinity of the equilibrium temperature. This is, however, unimportant in the case of a hot wire relay of the Sunvic type, which, in any case, does not operate instantaneously.
(<u>Note</u>: As the phase change from the grid of V_1 to the grid of V_3 is $\pm 360^\circ$, the phasing control, mentioned by Sturtevant, has been omitted.).

As may be seen from the foregoing, the construction of this relay has involved a considerable amount of work. It is felt, however, that the results obtained have justified this. If due precaution is taken to keep the on and off periods of the relay approximately equal (by appropriate setting of the three-heat switch), the room temperature does not very by more than 0.06°C., <u>even when two people enter the room</u>. In the second place, once the bridge and temperature adjustments have been set, they may be left untouched for very long periods. The room may be put into operation simply by switching on the power to switchboard 4, and allowing the room to run for a few hours to reach equilibrium. It is obvious that this method of temperature control is far more accurate, and much more convenient than the old one.

The main chassis, L-2, and the Sunvic relay and pilot light, are mounted on a thick wooden board, which is secured to the West wall just above the balance slab (See Plate I).

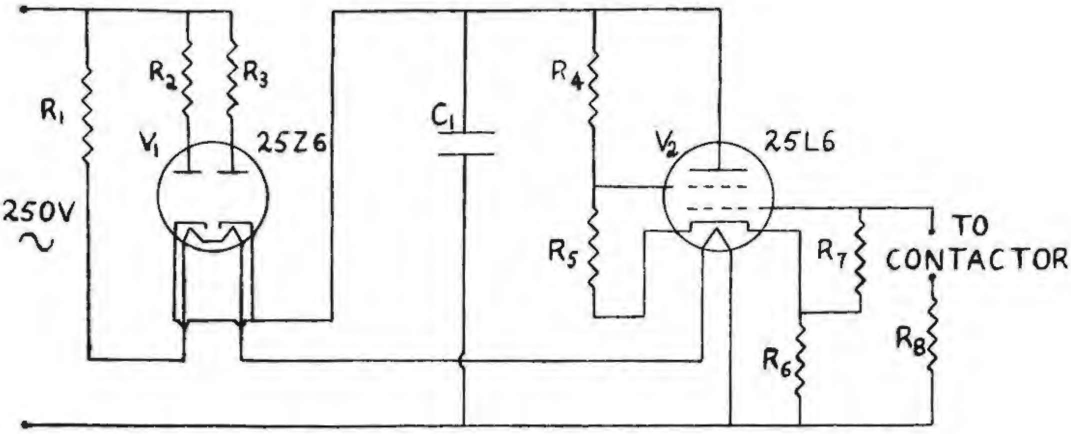

FIG. V(A.) CIRCUIT OF THERMIONIC RELAY

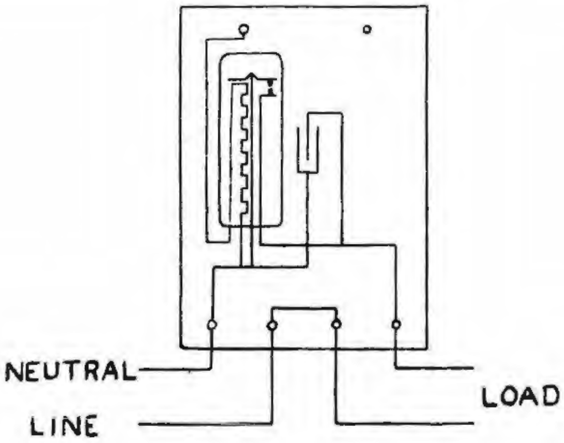

FIG. V(B.) SUNVIC RELAY

FIG. VA. CIRCUIT OF THERMIONIC RELAY.

R_1 = 75 watt lamp;

R_2 = 200 ohms;

R_3 = 200 ohms;

R_4 = 100 K ohms;

R_5 = 15 K ohms;

R_6 = relay heater;

R_7 = 2 M ohms;

R_8 = 200 K ohms.

C_1 = 8 μF

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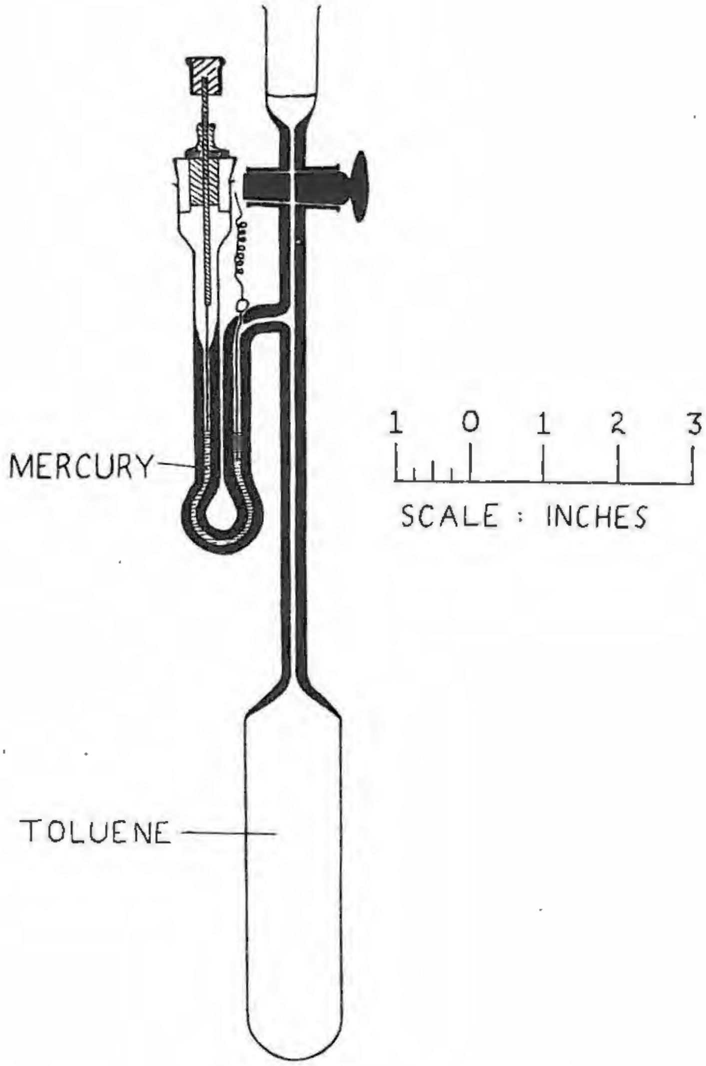


FIG.V(C) THE THERMOREGULATOR

D. CONTROL OF THERMOSTAT TEMPERATURE.

The Regulator (See Fig. V (C))

The regulator used by Gledhill has proved satisfactory, and is used here, but with one slight modification : in order to increase the sensitivity of the instrument, loosely packed, fine copper wire was placed in the toluene bulb.

The Thermionic Relay (See Fig. V(A))

The Gledhill circuit had to be modified to operate a Sunvic relay, which requires a much larger control current than the Struthers-Dunn relay, which he used. To carry this current, the 6 C 5 was replaced by a 25 L 6 (V_2), a beam tetrode. The potential of the screen grid, relative to the cathode, is kept nearly constant by the potentiometer arrangement $R_4 R_5$. A further difference is that the Struthers-Dunn relay switches off the heater current when the control current flows; it is necessary for the Sunvic to switch on the heater when the control current flows. This was accomplished by using the alternative arrangement of resistors as described by Waddle and Saeman (9). The relay is mounted above the thermostat (see plate X), and voltage dropping lamps mounted beneath the c-t room.

E. THE CONDUCTANCE BRIDGE.

There is little doubt that the Gledhill bridge is capable of a precision of 0.001%. It is, however, a delicate task to balance it to this accuracy. As stated before, in designing the new bridge, more attention has been paid to increasing the ease of manipulation than to improving the precision of measurement. In the first place, all controls are easily accessible, and, in the second, the telephones have been replaced by a visual detector, which is less tiring to the observer. Furthermore, an attempt has been made to improve the purity of the wave form of the oscillator and the general selectivity of the amplifier, with a view to increasing the general sensitivity of the bridge. It is an easy matter to balance to 0.001%, if the bridge is sensitive to smaller changes.

General Allocation of Space.

The bridge, which is 4' wide, and the two thermostat tables occupy the whole of the South wall (see Plate II). To accommodate the oscilloscope, the bridge had to be at least 18" deep, and, as wood 1' wide was available, it was made 2' deep. To make all terminals within easy reach of the observer, the height was restricted to 5'. A space of 2' x 2' x 2' was left in the centre of the bridge for the legs of the observer. The whole framework was mounted on 4 heavy casters, to make for easy movement of the bridge. This raised its height by 4".

The oscilloscope is housed in the centre of the bridge, at a height of 3' above the floor. In this position, the screen is slightly below eye-level, which experience has shown to be the optimum position. The dimensions of the oscilloscope and its compartment are respectively, 14¾" x 8¾" x 19½", and 17" x 10" x 24"; the extra height of the latter is to allow for free circulation of air, as the oscilloscope dissipates 90 watts. The general allocation of the remaining space may be seen from plate II. The amplifier is housed in the left "leg", which measures 24" x 11½" x 24"; the oscillator is in the right "leg", which is of the same size. The space (33" x 18" x 24") to the left of the oscilloscope contains the ratio arms, and the resistances and condensers of the measuring arm, except the 10,000 ohm decade. This is contained in the space (14½" x 27" x 24") above, and to the right of the oscilloscope. The remainder of the space (18" x 17" x 24"), to the right of the oscilloscope, is used for the Wagner Earth Components.

Both the amplifier and oscillator units are supported on boards attached to their respective front panels; the boards can slide into and out of the bridge framework, as they merely rest on wooden strips, fixed to the framework. All interconnecting leads are of such a length, that the units may be withdrawn a few inches, and the leads then disconnected. This design was developed to facilitate removal of the units for repair work.

Shielding.

The need for some form of electromagnetic shielding, to prevent interaction between oscillator and amplifier, is apparent. Complete shielding is, however, very difficult to achieve, and it is therefore important to keep the inductance in the oscillator circuit down to a minimum. Jones and Josephs (1) found there was considerable coupling between their oscillator and amplifier (the oscillator contained inductance in the resonant circuit, and the bridge was coupled to the amplifier by means of a transformer). They therefore separated the oscillator from the main bridge assembly by 10'. Luder (10) also did this, although he did not use an output transformer. It is apparent that he could not have realised that there was very little coupling present, as Gledhill (3) showed by practical experiment that this large separation was unnecessary. In the present bridge, the two units are separated by only 2',which has proved to be quite sufficient, and allowed all controls to be made easily accessible.

To reduce A.C. pickup, and to eliminate hand capacity effects, electrostatic shielding is essential. The shielding is complete if the unit, to be shielded, is enclosed in a metallic box, which is maintained at a fixed potential (usually earth). The best materials for electrostatic shielding are the good conductors. As a supply of sheet copper and aluminium was available, both were used for this purpose. Each bridge compartment is completely lined; between any two adjacent compartments there are thus two layers of metal. The shielding is, therefore, almost certainly complete.

The metal sheets were cut somewhat wider than the compartments which they were to line, and were bent over at the front and back. In this way, electrical contact is ensured between all shielding, including that which is screwed on at the back and front of the bridge.

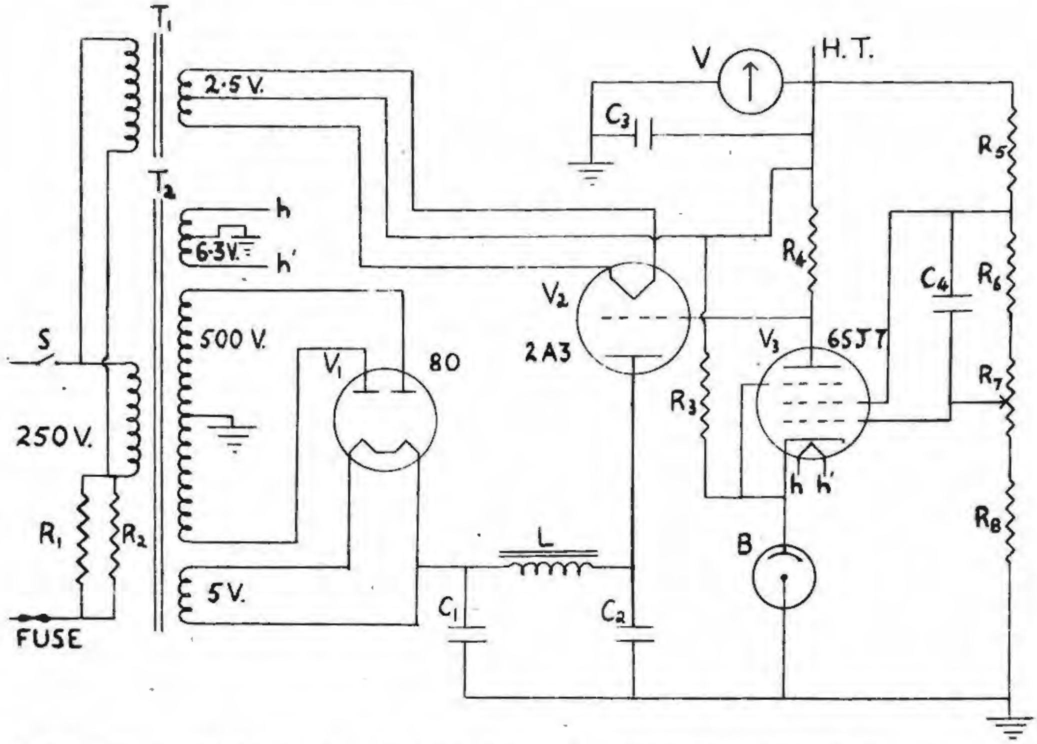


FIG.VI(A) CIRCUIT OF REGULATED POWER SUPPLY

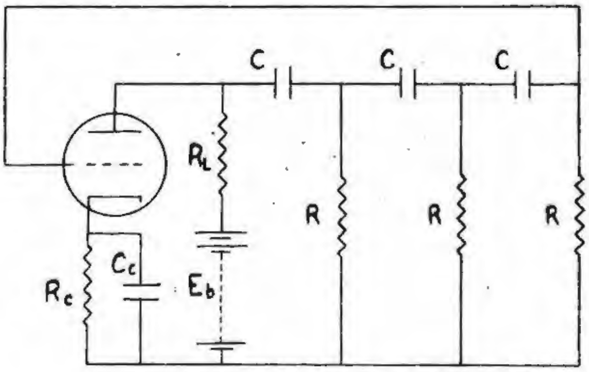


FIG.VI(B) SIMPLIFIED CIRCUIT OF PHASE SHIFT OSCILLATOR

FIG. VIA. CIRCUIT OF POWER SUPPLY.

R_1 = 250 ohms;
R_2 = 250 ohms;
R_3 = 2M ohms;
R_4 = 0·5M ohms;
R_5 = 20K ohms;
R_6 = 10K ohms;
R_7 = 10K ohms;
R_8 = 5K ohms.
V = voltmeter, 0–300V.

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.

……………………………

The Source of A.C. to the Bridge.

(1) The Regulated Power Supply. (See Fig. VI A).

This is essentially the same as that described by Gledhill, except for one or two minor alterations.

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

b) 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 the 6SJ7 to the control grid, were introduced as there was a tendency for the power pack to oscillate.

c) the regulated H.T. was connected to the cathode of the 6SJ7 through a 2 Megohm resistor, R_3, for the following reason; without this resistance, when the value of the unregulated H.T. approached the value of the regulated H.T., the current through the 6SJ7 and neon bulb was very small, and the latter tended to stop conducting. With R_3 in place, the small current, which flows through the neon bulb from the H.T. line, is sufficient to maintain the discharge. This improves the regulation at low values of the unregulated H.T. The oscillator is designed to run off 250 V.; by adjusting the variable resistance, R_7, the regulated H.T. can be set to this value.

(iii) The Oscillator. (See Fig. VII).

The polarisation correction, for the resistance (R) of a cell, is obtained by plotting R vs $f^{-1/2}$ where f = frequency of operation, and extrapolating to $f^{-1/2} = 0$ (as suggested by Jones and Christian (20). Experience with the Gledhill bridge has shown that, to obtain satisfactory extrapolation, at least 5 frequencies are desirable. These should be chosen so that the five points of the above graph are spaced equally along the X axis.

i.e. $(fn+1)^{-1/2} - (fn)^{-1/2} = (fn)^{-1/2} - (fn-1)^{-1/2}$ - (A).

The lowest frequency is usually fixed at 500 c.p.s. The upper frequency limit should not greatly exceed 2000 c.p.s., as the sensitivity of the ear falls off appreciably above this limit (Telephones are used in the bridge as an alternate means of detection). With these two limits, the five frequencies satisfying (A) are

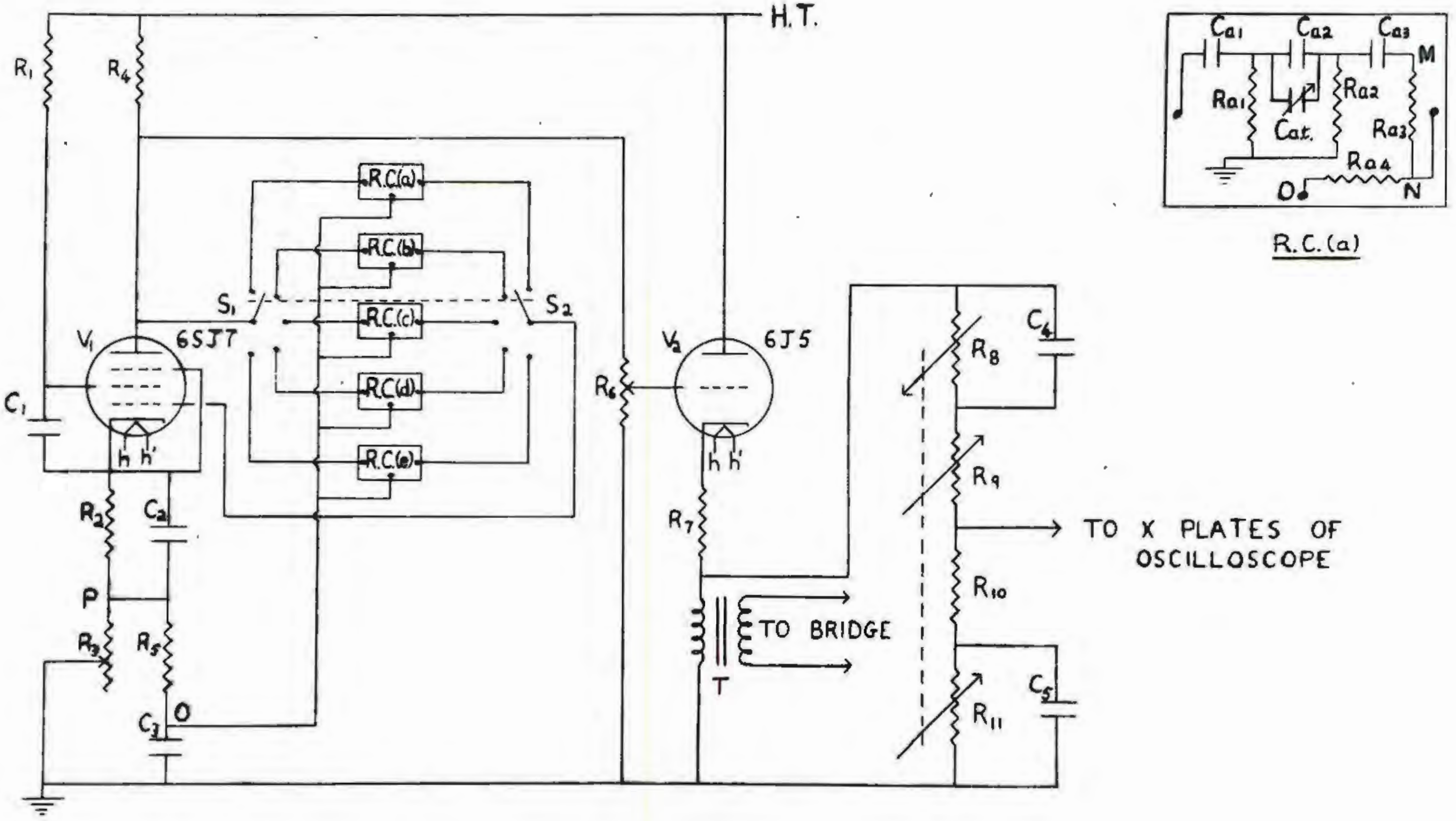
861

500, 653, 890, 1280, 2000.

It is much easier to adjust the oscillator frequencies to exact harmonics of the mains (see later), and the final frequencies decided upon were

500, 650, 900, 1300, 2000.

The oscillator is of the standard resistance -



R.C.(a)

FIG.VII CIRCUIT OF OSCILLATOR

FIG. VII. CIRCUIT OF OSCILLATOR.

R_1 = 250K ohms;
R_2 = 200 ohms;
R_3 = 1000 ohms;
R_4 = 50K ohms;
R_5 = 25K ohms;
R_6 = 250K ohms;
R_7 = 500 ohms;
R_8 = 250K ohms;
R_9 = 250K ohms;
R_{10} = 2·5K ohms;
R_{11} = 250K ohms;
Ra_1 = 210 ohms;
Ra_2 = 210 ohms;
Ra_3 = 70 ohms;
Ra_4 = 140 ohms;
Rb_1 = 175 ohms;
Rb_2 = 175 ohms;
Rb_3 = 28 ohms;
Rb_4 = 108 ohms;
Rc_1 = 135 ohms;
Rc_2 = 135 ohms;
Rc_3 = 12 ohms;
Rc_4 = 97 ohms;
Rd_1 = 145 ohms;
Rd_2 = 145 ohms;
Rd_3 = 0 ohms;

C_1 = 0·1 μF ;
C_2 = 8 μF ;
C_3 = 0·5 μF ;
C_4 = 0·01μF ;
C_5 = 0·01μF ;
Cat = 100 pF ;
Cb = 100 pF ;
Cct = 100 pF ;
Cdt = 100 pF ;
Cet = 100 pF ;
T = bridge transformer
Ca_1 = 550 pF ;
Ca_2 = 550 pF ;
Ca_3 = 550 pF ;
(a = 500 c.p.s.)
Cb_1 = 500 pF ;
Cb_2 = 450 pF ;
Cb_3 = 500 pF ;
(b = 650 c.p.s.)
Cc_1 = 410 pF ;
Cc_2 = 420 pF ;
Cc_3 = 420 pF ;
(c = 900 c.p.s.)
Cd_1 = 250 pF ;
Cd_2 = 250 pF ;
Cd_3 = 300 pF ;

$Rd_4 = 110$ ohms; (d = 1300 c.p.s.)

$Re_1 = 160$ ohms; $Ce_1 = 250$ pF;

$Re_2 = 100$ ohms; $Ce_2 = 160$ pF;

$Re_3 = 0$ ohms; $Ce_3 = 200$ pF;

$Re_4 = 205$ ohms; (e = 2000 c.p.s.)

capacity phase shift type (11), as shown in Figs. VI B and VII. An oscillator of this design is capable of giving a very pure wave form of fairly stable frequency, if reasonable care is taken in its construction. To obtain the required purity of wave form, the feedback should be adjusted so as to be just sufficient to maintain stable oscillation. This is done in two ways :

(a) a fixed coarse adjustment, built into each resonant circuit

(b) a variable fine adjustment, built into the cathode circuit, which operates at all frequencies.

Adjustment (a) consists of a potentiometer arrangement in the third leg of the resonant circuit (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 resonant circuits connected in the normal fashion (Fig. VI B), the amount of degeneration required to give a pure wave form varied greatly with frequency, being lowest at the highest frequency. Adjustment of the ratio NO : MO 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 at the other 4 frequencies. This was done by trial and error. If

If the adjustment is done with reasonable care, the oscillator can be made to give a pure wave form on all 5 frequencies, on one setting of R_3. This makes the bridge much easier to operate : R_3 need be adjusted only infrequently (e.g., when tube characteristics have changed due to age, etc.).

Adjustment (b) is the variable resistor (R_3) in the cathode of the 6SJ7 (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, point O will be at the potential of point 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. The value of this potential will be proportional to R_3, as the tube current remains practically constant. Hence the degeneration is proportional to the value of R_3

The frequency of oscillation is given by

$$f = \left[2\pi \; CR \; (6 + 4 \; R_1 \; / R)^{1/2} \right]^{-1} \qquad (B)$$

where $R\,1 = \dfrac{R_L . R_p}{R_L + R_p}$, and R_p = A.C. resistance of the tube.

(other symbols are clear from Fig. VI B).

Owing to stray capacities in the wiring, and the large tolerance of the components used, it was found that formula (B) is only approximate. The adjustment to the desired frequencies was made by trial and error. In order to adjust the frequencies accurately, a 100 p.F. trimmer condenser, Ct, was placed in each resonant circuit. The adjustment to the desired frequency is done with the aid of the oscilloscope, using the method of Lissajous figures. (a 50 cycle voltage is applied to the X plates, and the oscillator output to the Y plates).

The 6 J 5 tube (V2) is included as a buffer tube, to prevent changes in loading from affecting the frequency and stability of oscillation. Owing to the large amplitude of oscillation (± 60 volts), it is not a disadvantage if the amplitude is decreased considerably, i.e. if the 6 J 5 has an amplification factor of less than 1. Accordingly, this tube is connected up as a cathode follower (12), which has the advantage of combining a very low output impedance with a very high input impedance. Even using this arrangement, an output of 8 volts is easily obtainable. The bridge supply voltage should be in the neighbourhood of 2 volts, and for this reason, the General Radio bridge transformer, T (type 578 - B), is connected to step down the voltage to 2 volts. This is in antithesis to the usual procedure of stepping up the voltage to 2, (e.g. Luder (10), Gledhill (3)), but it has a distinct advantage : the impedance, Zin, across the primary terminals of a transformer is given by

$$Zin = n^2 . Z\ out$$

(where n = ratio of number of turns of primary to secondary

Z out = impedance across the secondary).

When the voltage is stepped down,

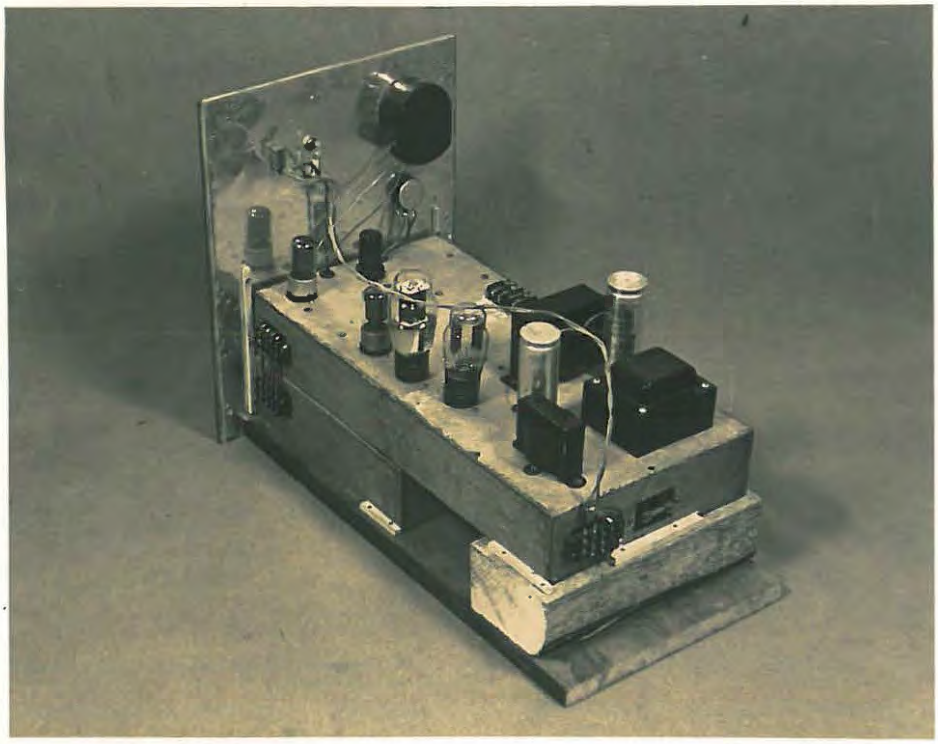
$n = 4$, and $Zin = 16. Z\ out$

When the voltage is stepped up,

$n = \frac{1}{4}$, and $Zin = {}^{1}/_{16}\ Z\ out$.

The former is obviously superior, as a very low impedance can be measured without overloading the oscillator : 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 voltage, supplied to the transformer, was taken from the cathode of the 6 J 5 through a condenser, distortion of the wave form resulted. This was overcome by connecting the transformer primary in series with the cathode resistor.



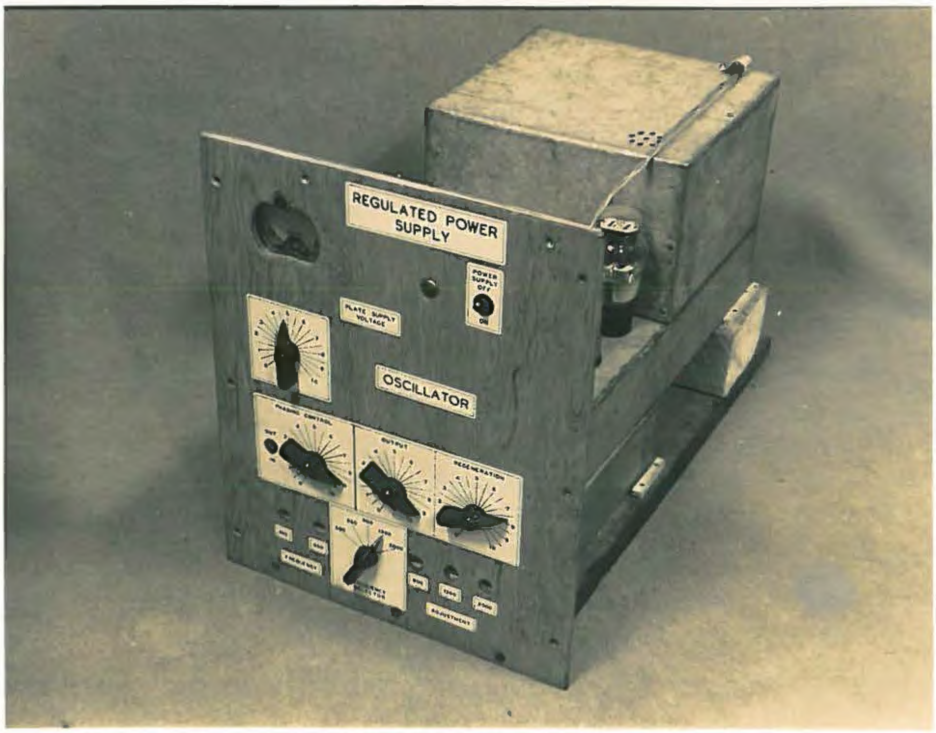

REGULATED POWER SUPPLY
POWER SUPPLY OFF
ON
PLATE SUPPLY VOLTAGE
OSCILLATOR
PHASING CONTROL
OUT
IN
OUTPUT
REGENERATION
FREQUENCY
800
1200
2000
ADJUSTMENT

PLATE IV

The Phasing Device consists of the network R_8, R_9, R_{10}, R_{11}, C_4 and C_5. In the two extreme settings of the ganged potentiometer, the phase changes of the output voltage are $+ 85^\circ$ and -81°. The use of the device will be explained later.

Mechanical Construction.

The oscillator and power supply are built on the chassis (see plate IV). In order to keep A.C. pickup at a minimum, the power supply is shielded from the rest of the circuit with gauge 20 galvanised iron. Owing to the large number of components in the resonant circuits and the necessity for making the trimmers easily accessible, all these components are built into a separate chassis, mounted beneath the main chassis. This type of construction has the added advantage that the heat from the valves does not reach the components of the resonant circuits. Thermal drift of frequency is thereby avoided.

All controls are brought out onto the front panel : the power switch S, with pilot light; the plate supply voltage control, R_7, with voltmeter; the regeneration control, R_3; the output control, R_6; the frequency selector switch S_1 S_2; and the five frequency adjustments C at, C bt, C ct, C dt, C et.

The Amplifier.

It was clear from readings taken on the Gledhill bridge, that one of the chief factors limiting the sensitivity of balance is stray A.C. pickup from unshielded parts of the bridge e.g. the knife-switches. The effect is especially pronounced on the lowest frequency. Accordingly, an endeavour was made to improve the selectivity of the amplifier, and experiments were undertaken to build an amplifier employing a system of degenerative tuning. The following quotation, from a paper by H.H. Scott (13), describes the principle very clearly.

"The important characteristic of this circuit is that the gain of the system, to which it is tuned, is the same as the gain of the amplifier at that frequency without the degeneration; at other frequencies, the gain drops very considerably.

In its simplest form, the system consists essentially of an amplifier and a feed-back network, which may be a bridge or similar type of circuit which balances to a null at a predetermined frequency. At this frequency, accordingly, no voltage is fed back from the amplifier output to the input, and the normal gain of the amplifier is obtained. At frequencies above and below this null point, however, the circuit is arranged so that the voltage fed back through the degenerative network is applied to the amplifier input with such a phase relationship with respect to the original input voltage, that a considerable reduction of gain is produced".

(Note: The gain of an amplifier with feedback, A^1, is given by

$$A^1 = A.(1 + B A)^{-1}$$

where A = normal gain of amplifier

B = fraction of the output voltage fed back to the input.

(except in special cases, B is of the form $a + i b$)).

"Naturally, the amount of this reduction will depend on the propagation constants of the amplifier and degeneration circuits (A and B respectively), but it will readily be seen that, if the degeneration network balances to a sharp null, a sharply selected response can be obtained".

"When the amplifier, used in a selective system of this type, has a relatively low amount of gain, satisfactory operation can be obtained without any particular difficulties. Since, however, the selectivity increases almost directly with the gain, and it is frequently desirable to use a relatively high degree of amplification, obviously the net propagation characteristic (A B) of the amplifying and degenerative systems must be such that regeneration and consequent oscillation are not produced. With the simpler circuits, the most common source of trouble is regeneration either at the high or low end of the frequency range due to phase shifts taking place within the amplifier circuits themselves. For this reason, the amplifier should be designed to have a minimum of phase shift over a range somewhat exceeding the range of frequencies over which the system will be used, or means should be taken to correct this shift".

The network, on which experiments were carried out, is the familiar twin-T network. A complete theory of this network was worked out, taking into account small errors in component values, as it was impossible to obtain accurate components. (The general theory has been worked out by Stanton (14)). This theory showed that balance could still be obtained in spite of deviation from ideal values, provided one component were adjusted to an accurate value. At the same time, the selectivity of an amplifier of gain 10^6, tuned in this way, was calculated. It was found to be far greater than that desired, but it was realised that the selectivity could be reduced if necessary.

On connecting the network across the amplifier, the latter was found to oscillate, owing to phase changes taking place in it at high frequencies. These phase changes were sufficient to cause regeneration and consequently oscillation set in.

Scott (loc. cit.) did not appear to have this difficulty. The direct-coupled amplifier which he used would eliminate low, but not high, frequency oscillation. Accordingly, no work was done on this type of amplifier, which is, in any case, difficult to construct. On consulting the literature (e.g. Eastman (18)), it was found that very great care is required in the construction of an amplifier free of these phase changes.

At the same time, accurate measurements, at constant temperature, of the resistances available showed that the values of these changed by as much as 0.5% in 24 hours. This was due, presumably, to changes in humidity; the resistances were therefore dried in a desiccator, and coated with paraffin wax. There appeared to be certain improvements after this, but the results were inconclusive. They served to show, however, that protection against humidity is a matter of some difficulty. It is essential for this work to have accurate wire wound resistances, but these were unobtainable.

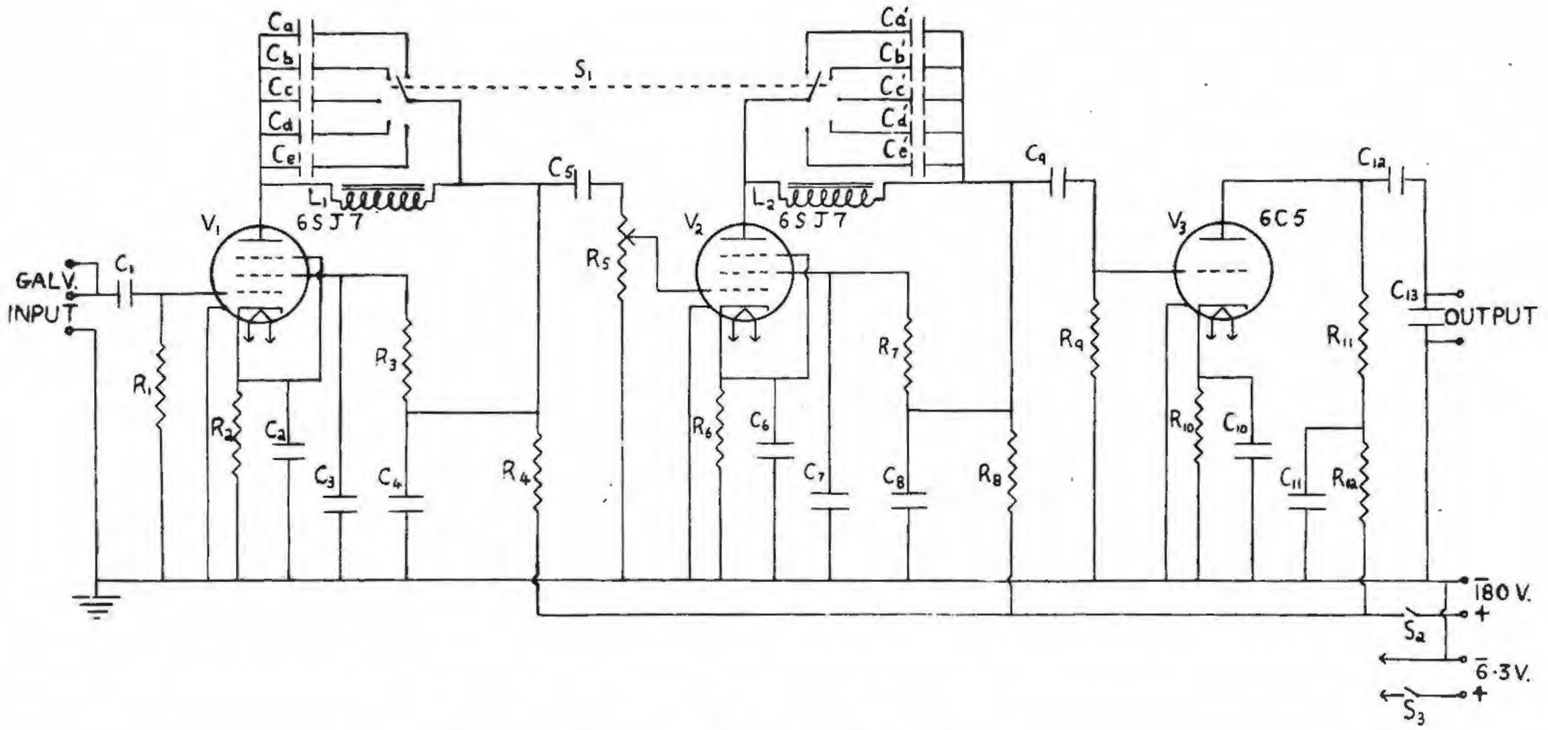


FIG. VIII CIRCUIT OF AMPLIFIER

FIG. VIII. CIRCUIT OF AMPLIFIER.

R_1 = 1.0 M ohms;
R_2 = 600 ohms;
R_3 = 0.5 M ohms;
R_4 = 5 K ohms;
R_5 = 1.0 M ohms;
R_6 = 600 ohms;
R_7 = 0.5 M ohms;
R_8 = 5 K ohms;
R_9 = 0.5 M ohms;
R_{10} = 3.5 K ohms;
R_{11} = 0.1 M ohms;
R_{12} = 5 K ohms;
L_1 = 10 henries;
L_2 = 10 henries;.

C_1 = 0·05 μF ;
C_2 = 8 μF ;
C_3 = 0·05 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} = 0.005 μF ;

Ca = 8550 pF ;
Cb = 5450 pF ;
Cc = 2700 pF ;
Cd = 1800 pF ;
Ce = 600 pF .

Ca' = 8400 pF ;
Cb' = 5300 pF ;
Cc' = 2600 pF ;
Cd' = 1450 pF ;
Ce' = 550 pF ;

……………………

For these reasons, further research on degenerative tuning was abandoned. There is little doubt, however, that, if put into operation successfully, this type of tuning would be very efficient.

In the absence of a better form of tuning, a three stage amplifier, with the first two stages tuned, was built; the tuning is done with parallel resonant circuits in the plate loads (see Fig. VIII). Although this does not give the desired selectiv~~f~~ity, it is a considerable improvement over an untuned amplifier. It has the following advantages :

a) there is no D.C. drop in the plate load, and therefore the plate is at full H.T. potential. Consequently, a fairly low H.T. supply (180 V.) may be employed.

b) owing to the large A.C. resistance of the parallel resonant circuit, in excess of 1 Megohm), a high gain per stage is obtainable.

The condenser values for each resonant circuit were obtained by inserting variable condensers into the circuits, applying a signal of appropriate frequency, and adjusting the condensers for maximum output. There is heavy decoupling in each plate circuit to prevent feedback from output to input through the H.T. line. The amplifier is run off batteries, so as to avoid A.C. pickup, and to avoid interaction between the oscillator

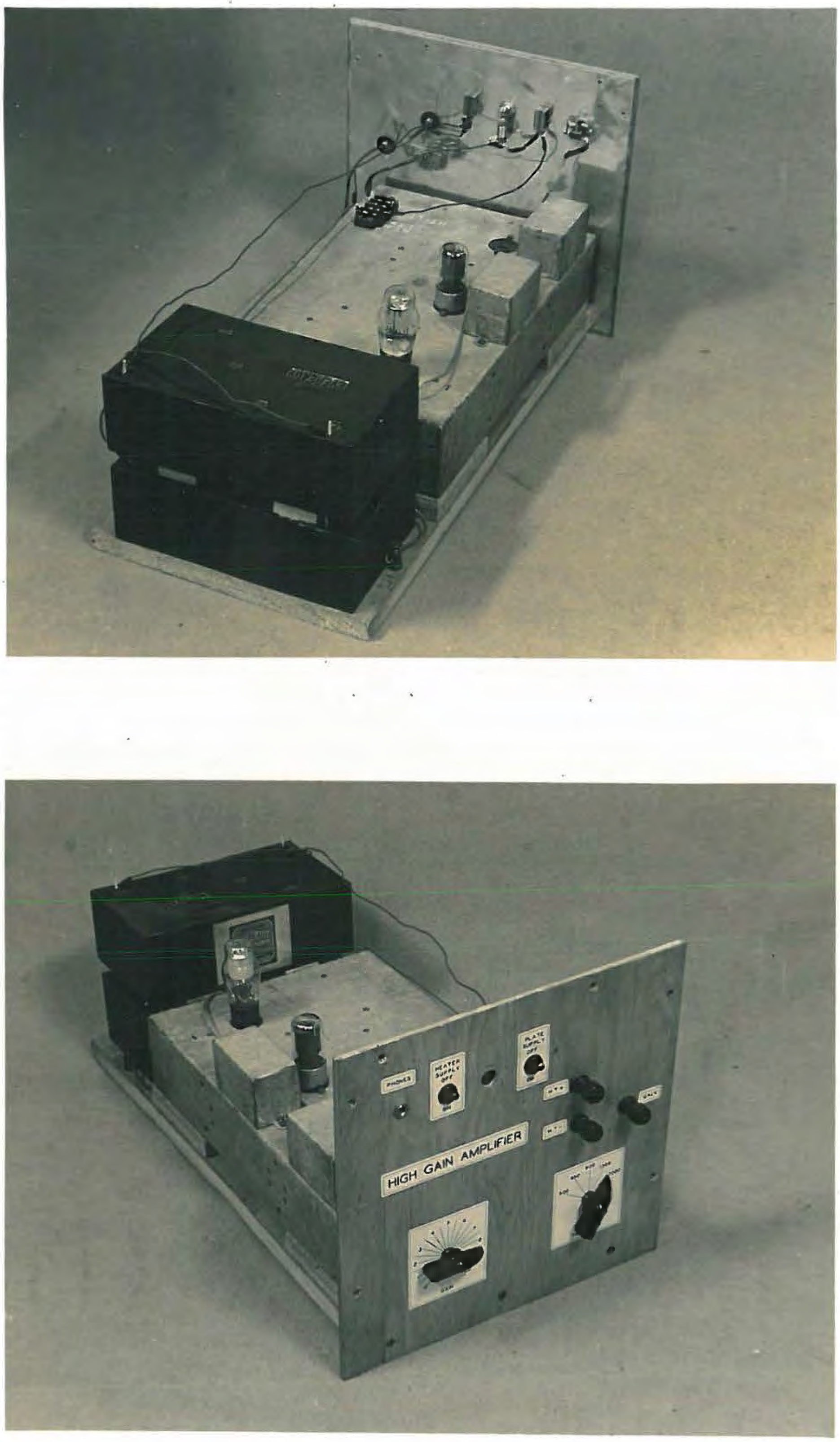

PHONES
HEATER SUPPLY OFF
ON
PLATE SUPPLY OFF
ON
HIGH GAIN AMPLIFIER
GAIN

PLATE V

and amplifier through the A.C. supply. The tube heaters are energised by a 6-volt lead accumulator, which is changed as required. A switch in the H.T. supply line enables the plate voltage to be switched off during the intervals between readings, so effecting considerable saving of the batteries; the current through the heaters is left on during these intervals, and this enables the amplifier to be brought into operation immediately.

Two terminals marked "H.T.+ " and "H.T.-" are brought to the front panel, so that the H.T. voltage can be checked without having to remove the amplifier unit from the bridge. A phone-jack is connected to the output of the amplifier, for use in the event of the oscilloscopes going out of order. For D.C. operation of the bridge, a terminal, marked "galvo" and connected to the amplifier input, is also included.

Mechanical Construction.

The amplifier is built on a chassis 10" x 16" x 3", and particular care has been paid to shielding. (see plate V). The two chokes (in the resonant circuits) are completely shielded, and the three stages are shielded from one another. In addition, all interconnecting leads between stages are shielded.

Jones, Mysels and Juda (16) have found that the first tube of a high gain amplifier often acts as a microphone, and the electric signals produced are amplified by the later stages of the amplifier. The simple device of mounting the amplifier on air-foam rubber has been found to reduce this sensitivity to noises considerably.

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

The Detector.

The detector used in the bridge is a cathode ray oscilloscope (type 208-B, Dumont). Its use in this connection was first suggested by Lamson (17).

The types of null detector, used in balancing impedance bridges, may be classified under three main headings:

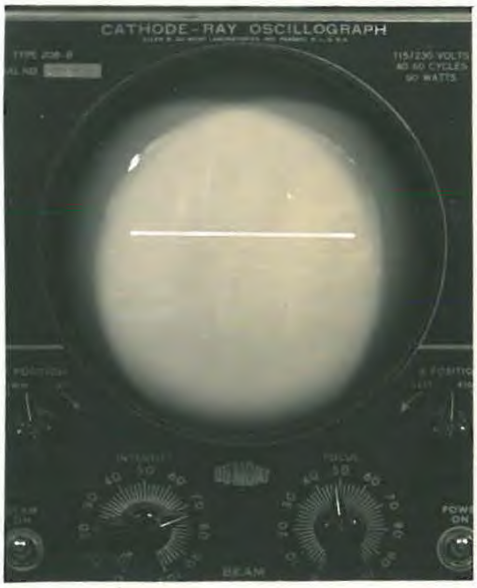
(i) Telephones
(ii) Galvanometer (either A.C. or with rectification, D.C.)
(iii) Electronic Visual Indicators.

The most common of these is, undoubtedly, type (i), the telephones, due to their low cost and relatively high sensitivity. They require a quiet environment for precise balance, and they are not phase discriminating (i.e. resistive and reactive components cannot be balanced separately).

Type (ii), the galvanometer, uses a visual indicator 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, manual operation is required to accomplish this phase shift, and the instrument is subject, at maximum sensitivity, to transient disturbances which are annoying, as time is required for the galvanometer to return to its original state.

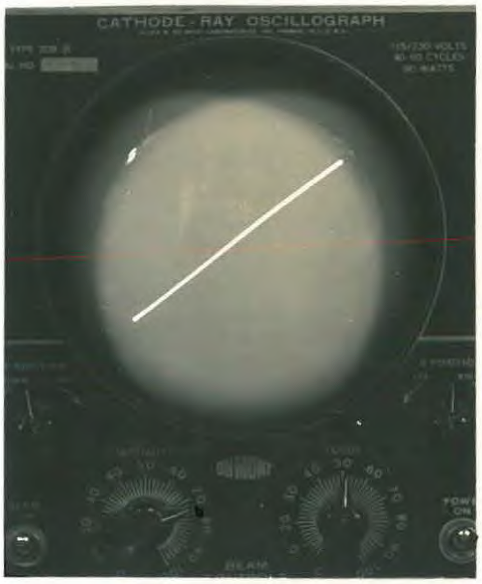
Type (iii) can be either a "magic eye" (similar to that used in radio) or a cathode ray oscilloscope.

Lamson (loc. cit.) has pointed out that the oscilloscope is superior to any other type of null detector, for the following reasons: the observations are visual and may therefore be carried on it the presence of external noise. Even in quiet surroundings, most people find visual observations less tiring than auditory observations. Moreover with the oscilloscope, extreme unbalance causes a harmless movement of the image off the screen, instead of a deafening noise in the case of telephones, and a surge of current in the case of a galvanometer, which will render it

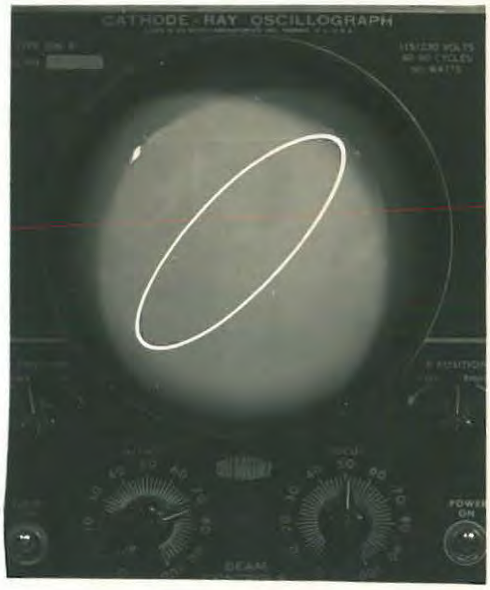


BALANCE

REACTIVE UNBALANCE



RESISTIVE UNBALANCE



COMBINED UNBALANCE

PLATE VI

inoperative for a considerable time.

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 A.C. source is fed to the X plates in correct phase, and the voltage from the detector terminals (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 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 (16) have applied this method of detection to a precision conductance bridge with very satisfactory results.

The Bridge Circuit. (Fig. IX).

The electrical circuit of the bridge is essentially the same as that employed by Gledhill, except for a slight difference in the Wagner Earth (see later).

The possibility of connecting the amplifier to the bridge by means of a transformer was considered as a method of obviating the necessity to balance the Wagner Earth accurately. This had been suggested by Gledhill (loc. cit.). However, it was decided to adhere to the method of separate terminal balance, as it is more accurate : a transformer with a low impedance primary will decrease the sensitivity of the bridge as the resistance being measured is increased. (Luder (10) mentions this effect). Also, the phase of the voltage applied to the detector terminals will vary as the resistance is increased, so making it impossible to find a satisfactory setting of the phasing control. These defects can be overcome by using a high impedance transformer, but this, however, is undesirable as it will increase the A.C. pickup and also the likelihood of interaction between oscillator and amplifier (See Astin (18)).

The only alternative is the use of a doubly shielded ungrounded amplifier as recommended by Dye and Jones (19). It was felt that the additional trouble involved in the construction of such an amplifier is not warranted by the small additional convenience obtained. For these reasons, the separate terminal balance method has been adhered to.

(Note: If there is interaction between the oscillator and amplifier, which produces a small voltage $\delta V(\Theta)$,

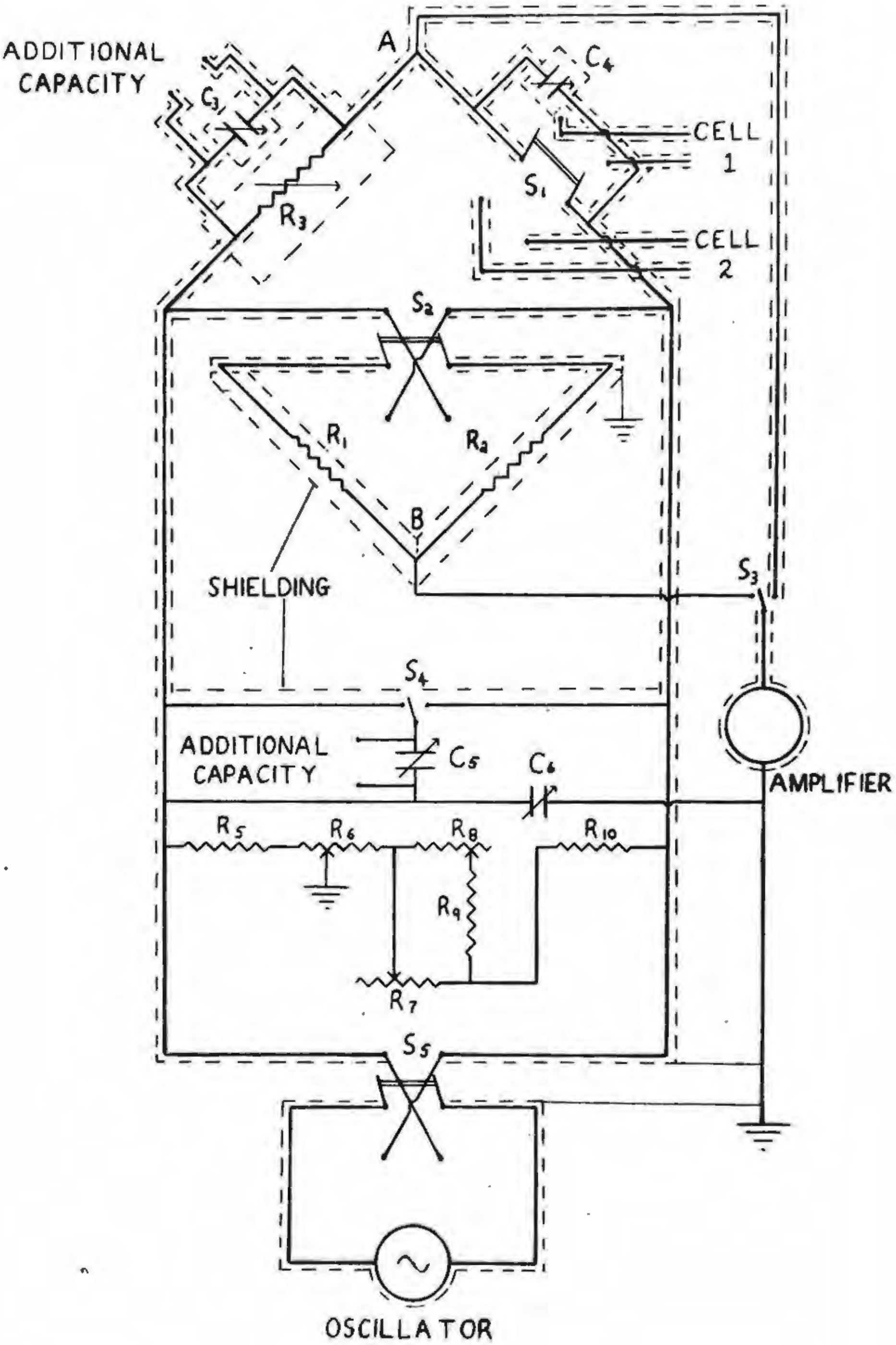


FIG IX CIRCUIT OF CONDUCTANCE BRIDGE

FIG. IX. CIRCUIT OF CONDUCTANCE BRIDGE.

R_1 = 10,000 ohms;
R_2 = 10,000 ohms;
R_3 = Measuring arm (max. resistance 111,111 ohms);
R_5 = 10,000 ohms;
R_6 = 1000 ohms;
R_7 = 50 ohms (max.);
R_8 = 1000 ohms (max.);
R_9 = 1000 ohms;
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.).

....

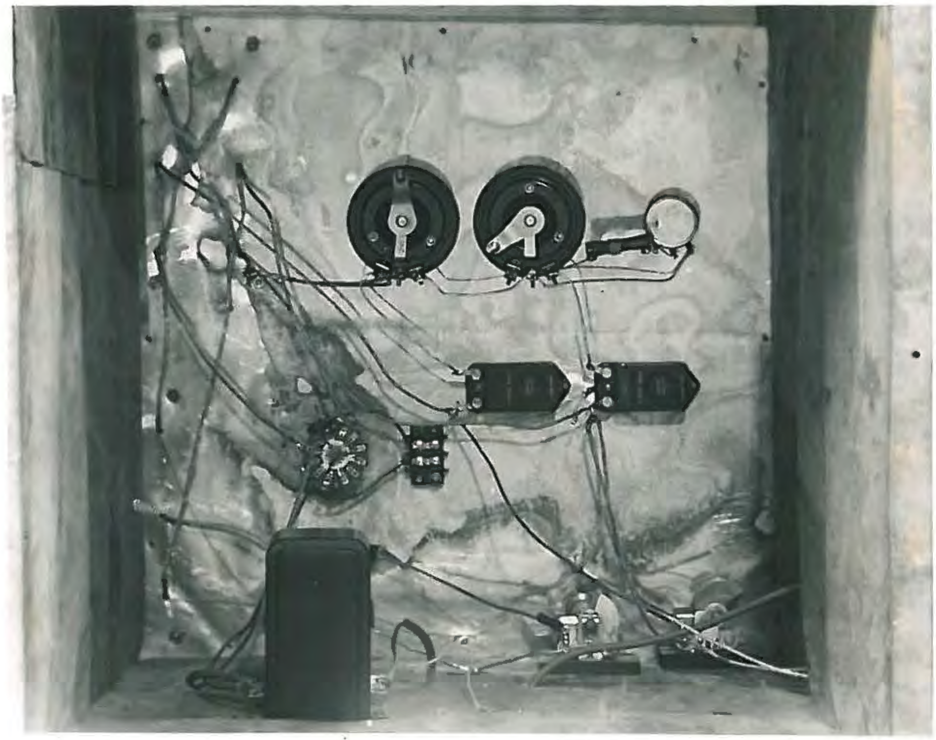
zero voltage can still be obtained by suitable adjustment of the bridge (so that the output voltage just balances the interaction voltage, i.e. it is equal to $\delta V(180^\circ + \theta)$. The pickup remains constant. Therefore, if separate terminal balancing is employed, only a small error is introduced, as V_B will still be equal to V_A i.e. the bridge itself will be accurately balanced (See Fig. IX). The error introduced if A and B are not at earth potential is, in any case, small, and if they are only at potential δV, it is neglibible.

With transformer coupling, however, $V_B - V_A$ will be equal to $\delta V(180^\circ + \theta)$, so that the bridge will not be accurately balanced. The superiority of separate terminal balancing is apparent.

Note on the knife switches used in the bridge circuit.

It was impossible to obtain knife switches with a distance of 1½" between contacts (the distance recommended by Gledhill). Accordingly, two dozen "Genalex" knife switches were ordered, and the arms and contacts removed from their bases. The arms were lengthened by rivetting onto them suitable lengths of 1/16" copper strip, and the join soldered to ensure good electrical contact. The arms and contacts were then rivetted onto ebonite bases at suitable distances apart. In this way, three double-pole double-throw, and two single-pole double-throw switches were made. (See plate VII). To minimise any possibility of leak across the handles of the former, these handles were constructed wholly of ebonite. The rivets holding the contacts of the switches extend to the bottom of the ebonite bases. Therefore, when the switches were fixed to the front panel of the bridge, they were mounted on ebonite washers, to prevent any leak across the surface of the panel.

It was necessary (see later) to construct eleven single-pole double-throw knife switches for the 10,000 ohm decade. Instead of manufacturing these singly, the arms and contacts were rivetted to a single board of ¾" ebonite, measuring 28½" x 12¾" (see plate IX). This method of mounting saved a lot of labour, and is also preferable for a reason, which will be given later. (<u>Note</u>: In designing the front panel, an effort has been made to place all knife switches near the outer edges of the bridge. In addition, where there are coarse and fine adjustments (of resistance or capacity) on a panel, these have been arranged, as far as possible, so that the coarse adjustment is nearer the outer edge of the bridge. With this arrangement, when making a final adjustment to the bridge, the hands of the observer are at considerable distances fromthe knife switches, so cutting down hand capacity effects greatly.)



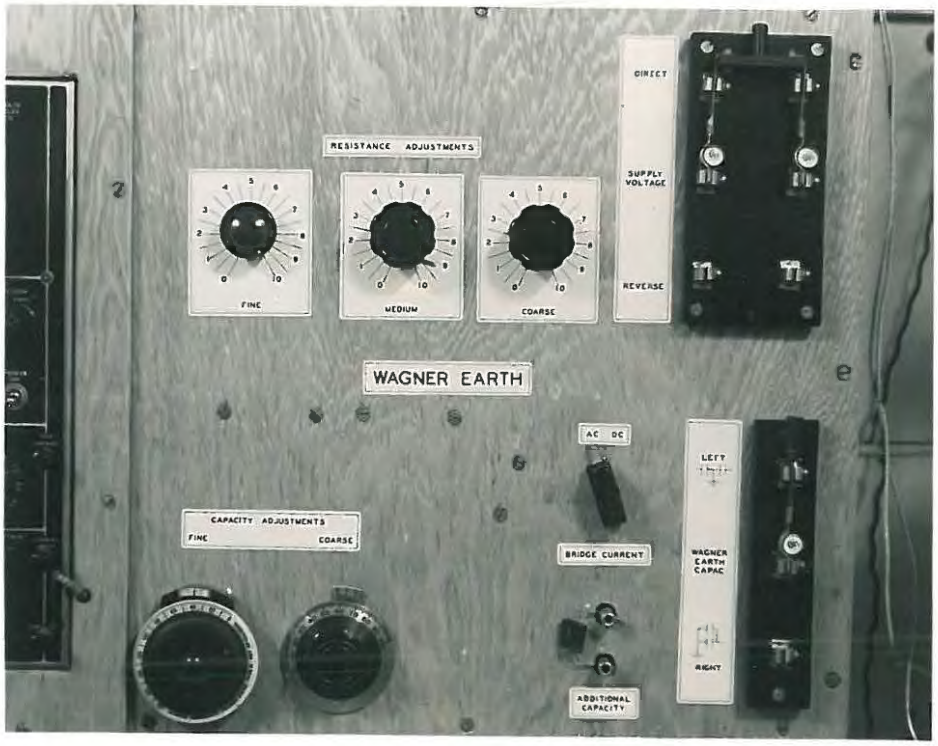

RESISTANCE ADJUSTMENTS
FINE
MEDIUM
COARSE
DIRECT
SUPPLY VOLTAGE
REVERSE
WAGNER EARTH
AC DC
CAPACITY ADJUSTMENTS
FINE
COARSE
BRIDGE CURRENT
ADDITIONAL CAPACITY
LEFT
WAGNER EARTH CAPAC
RIGHT

PLATE VII

The Wagner Earth.

The Wagner Earth panel (See plate VII) 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 screw 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 to right or left.

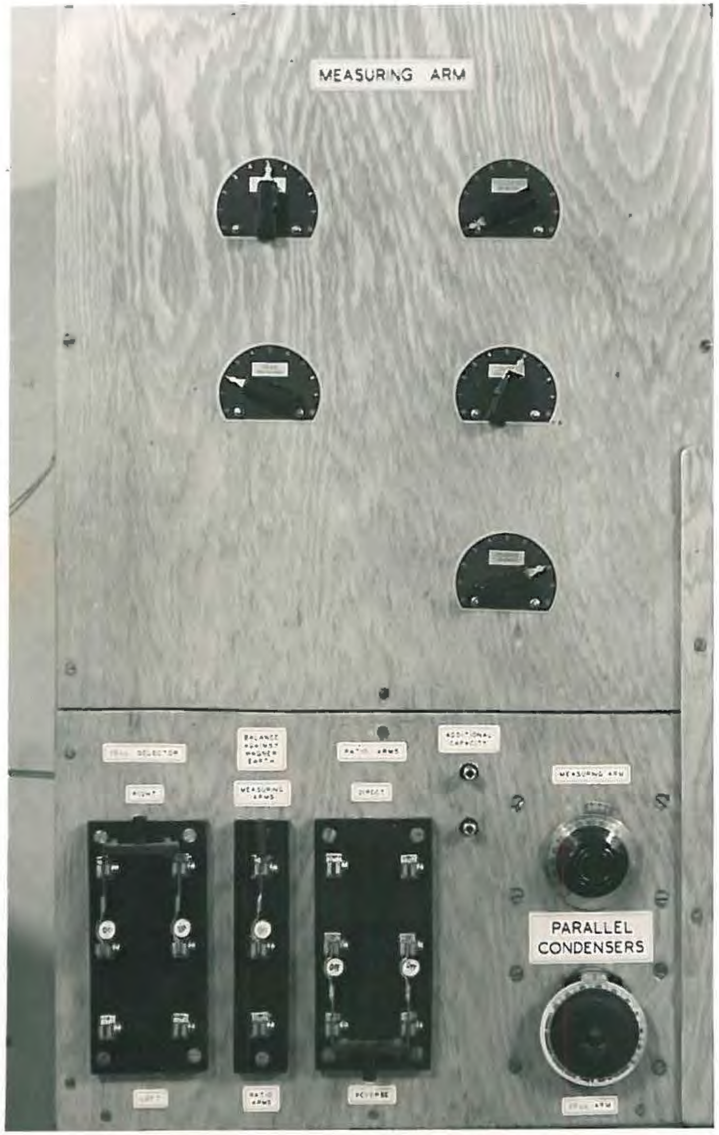
The coarse resistance adjustment (see Fig. IX) is a 1000 ohm potentiometer (R_6), the centre tap of which is the earthed point of the Wagner Earth; the medium resistance adjustment is a 50 ohm variable (R_7); the fine adjustment was intended to be a 2 ohm variable; unfortunately, this type of resistance is out of manufacture, and has been temporarily replaced by a fixed resistance of 1000 ohms (R_9) and a 1000 ohms variable (R_8) which are connected in series, and are in parallel with R_7. (The fine adjustment is essential because of the necessity to set the Wagner Earth with the same accuracy as the Bridge).

The coarse capacity adjustment is a 320 P.F. variable air condenser (C_5); the fine is of the same type and of maximum capacity 100 p.F. (C_5). Both are equipped with slow motion drive, that of the fine being extremely delicate.

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

The Components of the Wheatstone Net.

a) The Measuring Arm. The six resistance decades are General Radio types 510-A, -B, -C, -D, -E, and -F, and have 0.1, 1, 10, 100, 1000, and 10,000 ohm steps respectively. In accordance with the conditions laid down by Shedlovsky (2), all the resistances are mounted at a minimum distance of 2½" from shielding. In his own words : "this spacing proved to be sufficient, by actual test, to make the effect of screen capacity on the resistance negligible". For this reason, all the decades making up the measuring arm, R_3, have had their closely fitting shields removed. Except for the 10,000 ohm decade (which is connected in a special way - see later), all the decades are mounted on a subsidiary piece of ply-wood, situated 3" behind the front panel. In this position, the resistances are over 3" 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 ordered


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

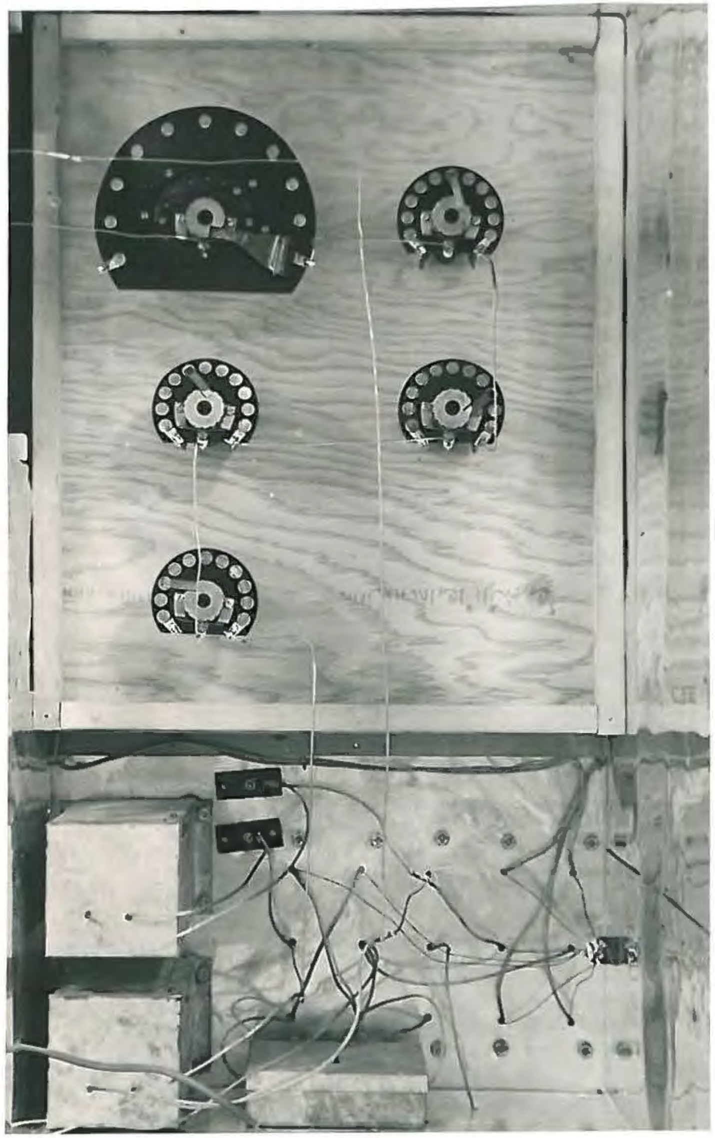


PLATE VIII

from the General Radio Company. (See plate VIII). (Note: Jones and Josephs (1), on empirical grounds, recommended that the distance between two binding posts, carrying between them a resistance, R, should be at least $0.04R^{\frac{1}{2}}$ cm. apart. This is in order to minimise errors due to leakage along the surface, actual loss in the dielectric, and capacitive shunt between the two terminals. The 0.1, 1, 10 and 100 ohm decades conform to the Jones and Josephs formula, but the minimum distance between contacts for a decade, with 1000 ohm steps, works out at about 1.3 c.m. This decade was therefore modified in the same way as described by Gledhill (3), as the method had proved very satisfactory in use. The radius of the switch was increased to 9 c.m., the studs spaced around the edge of the ebonite, and the resistances symmetrically mounted. (See Plate VIII)).

Calculation by the Jones and Josephs formula shows that the contact studs of a switch for the decade with 10,000 ohm steps should be at least 4 cm. apart, and, if there are 10 separate resistances, any terminals, across which the total 100,000 ohms will come, must be 13 cm. apart. A rotary switch, built to these dimensions, would be very unwieldy. To overcome this difficulty, Lu~~n~~der (10) designed a 10,000 ohm per step decade using knife switches; all the steps, not desired for a particular reading, are left out of the circuit completely. This design has been followed.

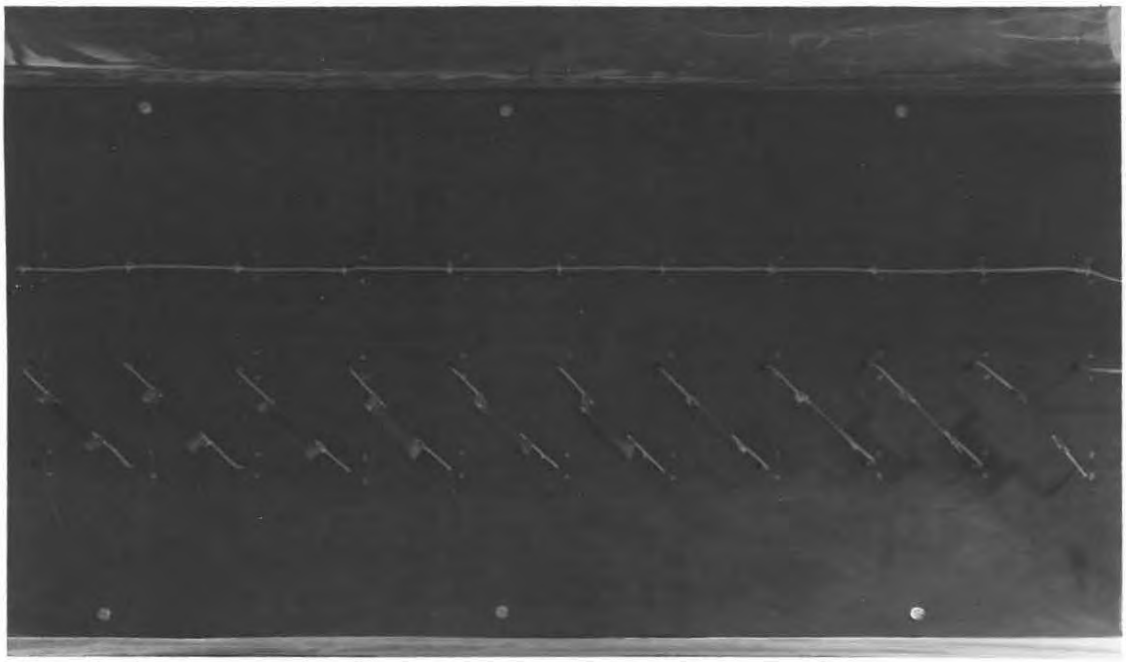
As previously indicated, the knife switches are mounted on a large board of ebonite, the distance between each switch being 4 cm. It should be noted that, as the switches are mounted directly on ebonite, the necessity for passing the leads (which connect the resistances to the contacts) centrally through the holes in the board falls away. The ebonite board is mounted at a distance of 5" behind the front panel. A section of the latter (23" x 10½"), immediately in front of the board, can be opened on hinges: this allows the knife switches to be operated (see plate II). When the appropriate setting of this decade has been obtained, the shielded "flap" is again closed.

b) <u>The Parallel Condensers</u> in the measuring arm (C_3) and the cell arm (C_4) are ordinary variable air condensers of maximum capacities 340 p.F. and 105 p.F, respectively. The final adjustment is always made with the smaller condenser, as more sensitivity can be obtained with it. There is a pair of plug-in points for the addition of fixed condensers in the measuring arm if the capacity of C_3 is not sufficient; the "additional condensers" are of a good quality mica type.

The variable condensers C_3 and C_4 are shielded separately in cases made of galvanised iron, each condenser being screwed onto an ebonite base which is fixed to the shielding case. (See plate VIII). The latter is bolted to the front panel. As the movable plates of the condensers are connected to the driving shafts, it is desirable that these be insulated from the slow motion drives, so as to avoid hand capacity effects. This has been done by extending the shafts with 1½" lengths of ebonite rod.

The calibration of the condensers was carried out as follows: the condenser in the cell arm was disconnected, and the cell leads connected to a General Radio 500 J resistor (10,000 ohms, non-inductive). A standard variable condenser was placed in parallel with the resistor, and the bridge balanced for various settings of the condenser in the measuring arm. In this way, the condenser, C_3, in the measuring arm was calibrated. The various condensers to be used as additional capacities were placed in parallel with C_3 (set to a specified value), and balance again obtained. This gave the value of these condensers. The condenser in the cell arm (C_4) was then reconnected, the standard variable condenser removed, and the bridge balanced for various settings of C_4. In this way, C_4 was calibrated.

This method of calibration eliminates any errors



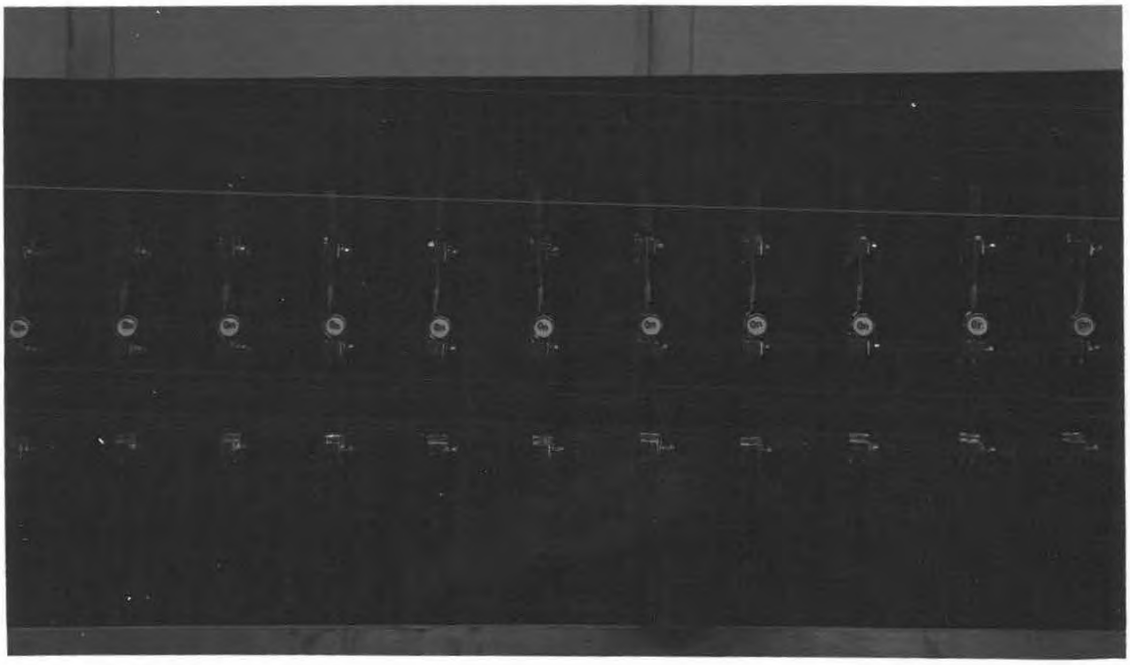


PLATE IX

due to stray capacities in the wiring, etc.

c) The Ratio Arms. It is clear that the ratio arms may be shielded closely, provided they are shielded symmetrically. Slight inequalities in the impedance of the arms are compensated for by the inclusion of the reversing switch S_2. The resistance of each of the arms, R1,and R2, is 10,000 ohms, the resistors being of the General Radio type 500J. The arms are mounted in a close-fitting, galvanised iron box divided into two halves, which are shielded from one another. To keep the connecting leads short, the ratio arms are mounted directly behind their associated reversing switch. (See Plate VIII). The other two switches, mounted on the front panel, are the cell selector switch S_1, and the switch S_3 which chooses either the measuring arm or ratio arms for balance against the Wagner Earth.

Insulation Tests.

The maximum resistance to be measured on the bridge is 10^5 ohms: the accuracy aimed at is 0.001%. Accordingly, to attain this accuracy, the insulation of components in the cell and measuring arms should be in excess of 10^{10} ohms.

The condenser leak method, for measurement of high resistance, is the most convenient for measuring insulation. Gledhill (3) stated that this method has the serious disadvantage of consuming considerable lengths of time, quoting a standard wait of 60,000 seconds. The necessity for such long periods of insulation was due to the fact that he used a standard condenser, C, of capacity 2 μF. As the time, t, required for insulation is proportional to C.R. (where R = the resistance under test), it is clear that t may be reduced by using a smaller condenser. One of capacity 0.338 μF enabled the insulation time to be cut down to 3,600 seconds, which is not unduly lengthy. 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 assembled (chosen at random). From the readings obtained, it was possible to check the validity of the Jones-Josephs formula for insulation. As found by Gledhill, it appears to be very generous indeed.

(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 proved to be well in excess of 10^{10} ohms.

It was unnecessary to test the insulation between the two terminals of the additional capacity plug in the

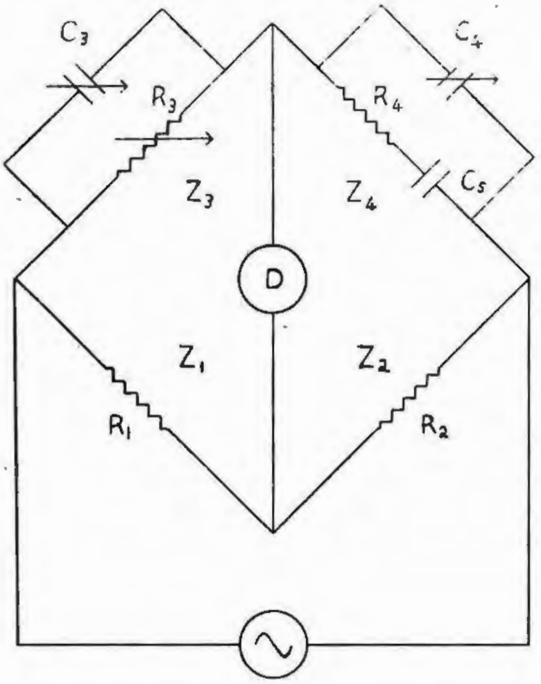


FIG.X(A) SIMPLIFIED BRIDGE CIRCUIT

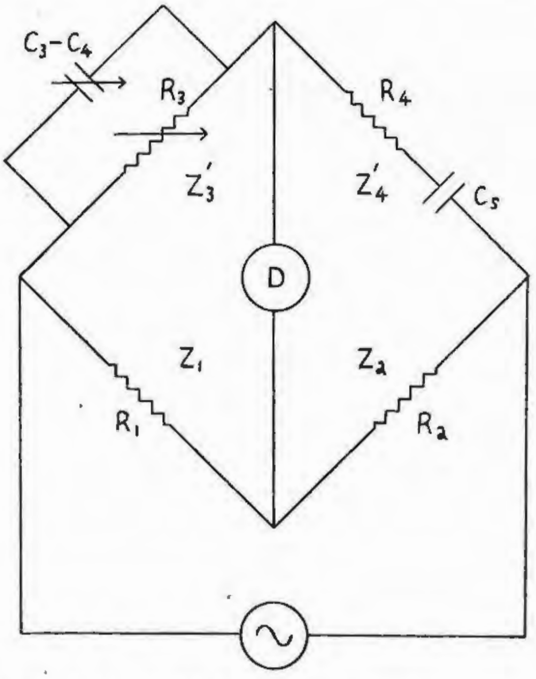


FIG.X(B) EQUIVALENT CIRCUIT

measuring arm. Each of these is mounted on a piece of ebonite, which is screwed to the shielding of the front panel. It is clear that each terminal may have a leak to earth, but there can be no direct leak between them. The leaks to earth will be balanced out when balancing the Wagner Earth. It is also unnecessary to test the insulation of the shielded wires, as mentioned by Gledhill, as the leaks will again be balanced out by the Wagner Earth.

Conditions for Balance of the Bridge.

It is generally assumed that the equivalent circuit of a conductivity cell can be represented by a resistance (the true resistance of the cell) and a capacity, C_s, in series with it. On this assumption, the circuit of the Wheatstone net is as shown in Fig. X A.

The general condition for balance is

$$\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4} \quad \text{where } Z = \text{impedance in each arm}$$

In each case, Z may be written

$$Z = r + jX \qquad \text{where } r = \text{resistance}$$
$$X = \text{reactance.}$$

Now $Z_1 = R_1$ and $Z_2 = R_2$

Also, $R_1 = R_2$

Therefore at balance $Z_3 = Z_4$.

It is obvious from the figure that the expression for

Z_4 will be a rather complicated one. There is, however, a method of simplifying the solution; imagine impedance Z_4 to consist of an impedance Z_4' with a capacity C_4 connected in parallel and similarly, imagine Z_3 to consist of an impedance Z_3' with a capacity $\underline{C_4}$ in parallel. It can at once be seen that Z_3' and Z_4' will be as shown in the second figure, X B.

We have that,

$$\frac{1}{Z_3} = \frac{1}{Z_3'} + j\,p\,C_4$$

$$\frac{1}{Z_4} = \frac{1}{Z_4'} + j\,p\,C_4$$

At balance, $Z_3 = Z_4$, and it is apparent from these equations that $Z_3' = Z_4'$, and that the solution of this equation will give the condition for balance of the bridge.

Let $C_3 - C_4 = C$

$$\frac{1}{Z_3'} = \frac{1}{R_3} + j\,p\,C$$

$$\therefore \quad Z_3' = \frac{R_3}{1 + j\,p\,CR_3} = r_3' + j\,X_3'$$

$$\therefore \quad r_3' = R_3\,\frac{1}{1 + p^2C^2R_3^2}\,,\quad X_3' = -\,\frac{pCR_3^2}{1 + p^2\,C^2R_3^2}$$

$$Z_4' = R_4 - j\,/\,p\,C_5 = r_4' + j\,X_4'$$

$\therefore$ $r_4' = R_4$ and $\qquad X_4' = -1\,/p\,C_5$

$\therefore$ putting $Z_3' = Z_4'$

gives $r_3' = r_4'$ (equating resistive components,

i.e. $$\frac{R_3}{1 + p^2 C^2 R_3^2} = R_4$$

It is found that the values of C, usually required, make the term $p^2 C^2 R_3^2$ small compared with unity. Using the binomial theorem to clear fractions, and ignoring powers of $p^2 C^2 R_3^2$ higher than the first, gives

$$R_4 = R_3 (1 - p^2 C^2 R_3^2) \qquad - (A)$$

Also $X_3' = X_4'$ (equating reactive components)

$$\therefore - \frac{pC R_3^2}{1 + p C^2 R_3^2} = - \frac{1}{p C_s}$$

$$\therefore C_s = (p^{-2} C^{-1} R_3^{-2} + C)$$

i.e. $$C_s = C (1 + p^{-2} C^{-2} R_3^{-2}) \qquad - (B)$$

(A) and (B), then, are the conditions for balance of the bridge, and must be fulfilled simultaneously.

The conditions for balance are, then,

$$\left.\begin{aligned} R_4 &= R_3 \quad (1 - p^2 C^2 R_3^2) \\ C_s &= C \quad (1 + p^{-2} C^{-2} R_3^{-2}) \end{aligned}\right\} \quad \text{where } C = C_3 - C_4 .$$

Manipulation of the Bridge.

1) Working on low gain of the oscilloscope, the values of R_3 (measuring arm resistance) and C_3 (measuring arm condenser) are adjusted until the image on the oscilloscope screen is approximately a horizontal straight line; additional capacities are put in parallel with C_3 if necessary.

2) The switch S_3 is then thrown over to "Ratio Arms", and the Wagner Earth resistance and capacity adjustments set to give an approximate balance, again using additional capacity if necessary.

3) S_3 is thrown back to "measuring arm", and R_3 and C_3 again set to give balance.

4) This alternate balance is repeated until an approximate balance is obtained where there is little change on switching S_3 from one position to the other.

5) At this stage, it is necessary to adjust the phasing device. S_3 is thrown over to "Ratio Arms", and a large unbalance in the resistive component obtained by changing the setting of the coarse resistor of the Wagner Earth. This will cause the horizontal image to tilt, and, in general, if the phasing control is incorrectly set, the image will be a tilted ellipse. The phasing control is adjusted so that the image collapses to a straight line. The coarse resistor is then returned to the position where the image once more becomes a horizontal straight line.

N.B. (i) the phasing control must be set for each operating frequency.

(ii) it is quite easy to see if the setting of the phasing control is incorrect: if it is, resistive changes will collapse or open the ellipse, as well as altering the slope of its horizontal axis. In the same way, capacitive changes will also alter the slope of the image.

6) Final balance is obtained when there is no change on switching S_3 from one position to the other. Obviously all fine adjustments are used for this purpose, and the oscilloscope turned up to high gain.

7) The supply voltage is reversed and balance again obtained.

8) The ratio arms are now reversed and balance obtained in the two positions of the supply voltage reversing switch.

This will give four readings for the frequency of operation, and the arithmetic mean of the values of R_3 and $(C_3 - C_4)$ is found.

9) The frequency selector switches are then altered to the next frequency, and the foregoing procedure repeated. This is done for the 5 frequencies giving, in all, a total of twenty readings for each resistance.

10) To obtain the true value of this resistance, R_4, the resistance values at each of the frequencies (p) are plotted against $p^{-1/2}$, and the line so obtained

extrapolated to infinite value of the frequency (in accordance with the Jones-Christian (20) method).

Performance of the Bridge.

The Bridge is very convenient to operate, and has proved to be very satisfactory. It has been established that a precision of 0.001% is easily attainable.

Note: The overall gain of the amplifier system, which includes the constructed amplifier and the Y plate amplifier of the oscilloscope, proved to be far greater than required. It was found desirable to dispense with one stage of the constructed amplifier; accordingly, the second stage has been eliminated, leaving a two-stage amplifier.

PART II.

ELUCIDATION OF CHROMIC SULPHATE COMPLEXES.

A. INTRODUCTION.

The remarkable colour changes undergone by solutions of chromium salts had become apparent at an early date. In addition, it had been established that there were considerable amounts of free acid in these solutions (e.g. Kruger (21)), and that if a solution of the violet sulphate were boiled, the colour of the solution changed over to green, the change being accompanied by a marked increase in the amount of hydrolysed acid in solution. Furthermore it had been noted (e.g. Werner and Gubser (22)) that solutions of the green chromic salts have conductivities much lower than those of the violet salts.

The unusual nature of these salts of chromium inspired a great deal of interest in them, and a vast amount of work has been carried out in this field. A brief review of the early work done has been given by Atkin and Chollet (23).

Recoura carried out an extensive series of experiments on many chromic salts, his work being reported mainly in Comptes Rendus (circa 1880). He concluded that, on boiling, a solution of violet chromic sulphate changed over to one of green basic sulphate and free sulphuric acid.

He regarded the change as

$$2\ Cr_2(SO_4)_3 + H_2O \rightarrow Cr_4O(SO_4)_5 + H_2SO_4\ ,$$

the amount of free acid being equal to $\frac{1}{6}$th of the total sulphate present. This observation was later confirmed by Whitney (24) who carried out conductometric titrations on chromic sulphate solutions with NaOH and $Ba(OH)_2$. He noted minima when NaOH equivalent to $\frac{1}{6}$th of the total sulphate had been added.

Richards and Bonnet (25) carried out dialysis experiments on violet and green chromic sulphates, and found that, whereas the violet solution dialysed unchanged, in the green, the ratio Cr/SO_4 diminished in the diffused portion and increased in the dialysed - an observation favouring the view that the change from violet to green involves a hydrolysis with the formation of free acid and a soluble basic salt. They confirmed the free acid hypothesis by cane sugar inversion experiments (the green solutions being much more acidic), and found that, if solutions (0.25N) of the green and violet salts were kept for 1 month at 30°C., the amount of free acid became the same in both cases, the acidity being greater at higher temperatures.

Miss Dougal (26) confirmed an earlier observation of de Boisbaudran (27) that the green solutions are less dense than the violet. This she attributed to the production of free H_2SO_4 during boiling.

Miss Graham (28) calculated the degrees of hydrolysis of the violet and green solutions from conductance measurements : the hydrolysis was found to increase with dilution, and to be greater in the case of the green. She also confirmed the observation of Richards and Bonnet that the violet and green solutions tend to the same equilibrium solution.

During this period Werner (29) had developed his theory of coordination to explain the structure of so-called "complex" or "molecular" compounds. The Werner theory was capable of throwing considerable light on the Chemistry of Chromium which has coordination number 6. If R is written as a univalent radicle ($R = Cl^-$ or $\frac{1}{2}\ SO_4^{--}$), it can be seen that there are four different salts theoretically capable of existence

$\left[Cr\ (H_2O)_6\right]^{+++}$	$3R^-$	violet	(no masking)
$\left[Cr\ (H_2O)_5\ R\right]^{++}$	$2R^-$	green	($\frac{1}{3}$ R masked)
$\left[Cr\ (H_2O)_4\ 2R\right]^{+}$	R^-		($\frac{2}{3}$ R masked)
$\left[Cr\ (H_2O)_3\ 3R\right]$			(all R masked).

The above formulae afford the evidence necessary to explain the low conductivity of the green solutions, and the low precipitatability of the radicle R from green solutions.

The theory is also capable of explaining the density decrease on boiling a violet solution. The change to green involves the transfer of water molecules from the complex into the solution, so increasing the volume of the latter.

On the basis of the Werner theory, Denham (30) criticised the conclusions of Recoura (loc. cit.); the formula $\left[CrO(SO_4)\right] SO_4$ he regarded as hypothetical and improbable. He carried out hydrolysis measurements at various concentrations, and also transport number and freezing point determinations, and concluded that the hydrolysis varied with the concentration of the solutions. From his own conclusions and those of Richards and Bonnett (loc. cit.), Denham suggested that the following changes took place on heating the violet solutions:

$$2Cr_2(SO_4)_3 \rightarrow \left[Cr_4(SO_4)_4\right](SO_4)_2 \quad \text{(polymerisation)}$$

followed by hydrolysis in two stages

$$\left[Cr_4(SO_4)_4\right](SO_4)_2 + 2H_2O \rightarrow \left[Cr_4(SO_4)_4\right](SO_4)(OH)_2 + H_2SO_4$$

which proceeds in fairly concentrated solutions up to $\frac{1}{40}$th molar, whilst at lower concentrations further hydrolysis takes place.

$$\left[Cr_4(SO_4)_4\right](SO_4)_2 + 4H_2O \rightarrow \left[Cr_4(SO_4)_4\right](OH)_4 + 2H_2SO_4$$

Lamb and Fonda (31), from conductivity measurements, determined the hydrolysis constants of violet and green chlorides, and pointed out the uncertainty of the methods previously employed in this connection.

In spite of the great amount of evidence in support of the Werner theory, Britton (32) still considers the evidence to be inconclusive. He claims that green chromic solutions contain basic chromium complexes which are micellar in structure, and constitute a colloidal electrolyte in which the cations are composed of chromium hydroxide and varying amounts of acid radicle, a portion only being ionisable. He considers that the results of Werner and Gubser (22) are inconvincing: to explain the low conductivity of a solution of the green chloride, and also its abnormal freezing point, these workers had postulated the formula $\left[Cr\ Cl_2.\ 4H_2O\right] Cl.\ 2H_2O$. However, they always found that, even in rapid estimations of Cl^- with $Ag\ NO_3$ at 0°C., more than one equivalent of chloride was always precipitated.

Weinland and Koch (33) studied the precipitability of the Cl^- using various silver salts. They found that all silver salts precipitated at least $\frac{2}{3}$ of the Cl^-, and that silver salts of weak acids increased the amount: the presence of strong acid in solution diminished the amount. N.H. Law (34) carried out conductometric titrations on the green chloride at 1.8°C., and found that only 1.5 equivalents of Cl^-

were precipitated. He claimed that the method was superior to gravimetric analysis, as adding $AgNO_3$ in bulk to a solution tended to precipitate all the chloride present.

Viscosity measurements carried out by Partington and Tweedy (35) indicated that the values of violet chloride solutions are much higher than those of the green solutions. They claimed that these results were in agreement with the formulae assigned by Werner; on the Britton theory the collidal solution (i.e. the green) should have displayed the higher value. Britton replied that, on the contrary, the results confirmed his own theory; the viscosity of metallic oxide hydrosols was usually little greater than that of water and the low viscosity of the green could have been caused by the appreciable amounts of free acid in solution.

More evidence against the theory of Britton was provided by the work of Howard and Patterson (36) who found that the effect of the violet and green salts on the critical solution temperatures of various mixtures is much greater than would be the case if the difference in the green and violet solutions were due to the presence of colloidal aggregates in the former. Colloids, per se, have usually a very small influence on the critical solution temperature. They claim that the method gives results more in accord with the Werner theory than do either freezing point or conductance measurements.

It is now generally conceeded that the Werner theory does afford the correct picture, but it must be remembered that hydrolysis in solution complicates the problem considerably. Most of the recent work on Chromium has been done by Leather Chemists, and it is significant that such well known workers as Stiasny and Gustavson have accepted the theory.

The Werner theory has been given a sound footing by the development of the modern electronic theory of valency, and, in particular, by Sidgwick's interpretation of the coordinate link. The electronic configuration of chromium (atomic number 24) is

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s$

and that of the chromic ion is

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

It may readily be seen that $S\ P_3\ D_2$ (4s, 4p, 3d) bond hybridisation can occur, so that in Cr^{+++} complexes the coordination number will be 6, and the resulting configuration octahedral.

The results of previous workers indicate that the formula of the violet salt is $[Cr(H_2O)_6]^{+++}\ 3F^-$ and that of the usual green salt is $[Cr(H_2O)_4F_2]^+\ F^-$; when each of these is dissolved in water, hydrolysis occurs with the formation of free acid and a soluble basic salt.

The purpose of the present work was to carry out conductometric titrations of NaOH into solutions of violet and green chromic sulphate in an endeavour to elucidate the nature of the complexes in solution.

In conductometric analysis, the graphs obtained are divided into a series of straight lines, and the points of inflection of these lines designate in general, the end of a specific reaction and the start of another.

PLATE X

B. DESCRIPTION OF APPARATUS.

(i) The thermostat.

The design of the thermostat may be seen clearly from plates X and XI. It is very similar to that built by Gledhill, although the dimensions throughout have been increased.

There are two vessels, the outer being of galvanised iron and the inner of sheet copper. The inner vessel is supported on three ebonite rods to prevent heat transfer from the bottom of the thermostat. The outer vessel is filled with water and is stirred continuously by a paddle stirrer, which is driven by a Garrard Gramophone Motor mounted on an iron framework above the thermostat (See plate X). No vibration is transmitted to the thermoregulator, which is mounted in the outer vessel on rubber bands. The heater, a 250 watt Cenco knife Type, is situated behind an asbestos baffle; after the temperature of the thermostat has risen to 25°C., the wattage supplied is cut down to approximately 40, by switching in voltage dropping lamps mounted beneath the c-t room. This makes the heater period roughly two minutes.

In spite of having taken the precaution of mounting the regulator as low as possible in the thermostat, it was still found than an observer near the thermostat affected the temperature slightly. For this reason, the regulator was screened from the front by a piece of highly polished aluminium.

The inner vessel, which accommodates the cell, is filled with paraffin according to the recommendation of Jones and Josephs (1). The paraffin is stirred with compressed air, which is first circulated through a copper tube in the outer bath. There is another coil in the outer bath which is used to bring to 25°C. the air used in stirring the contents of the cell. The temperature of the thermostat was read on a 16 - 34°C. thermometer immersed in the outer bath; it had been standardised against a N.P.L. thermometer. After the temperature had been set to 25°C., readings were taken on a Beckmann thermometer (also immersed in the outer bath) so as to determine accurately the actual variation in thermostat temperature.

Time	Temperature
9:00 a.m.	4.022°C.
9:30	4.022
10:00	4.024
10:30	4.023
11:00	4.022
12:00	4.022
2:00 p.m.	4.021
4:00	4.022
7:30	4.023
10:00	4.022

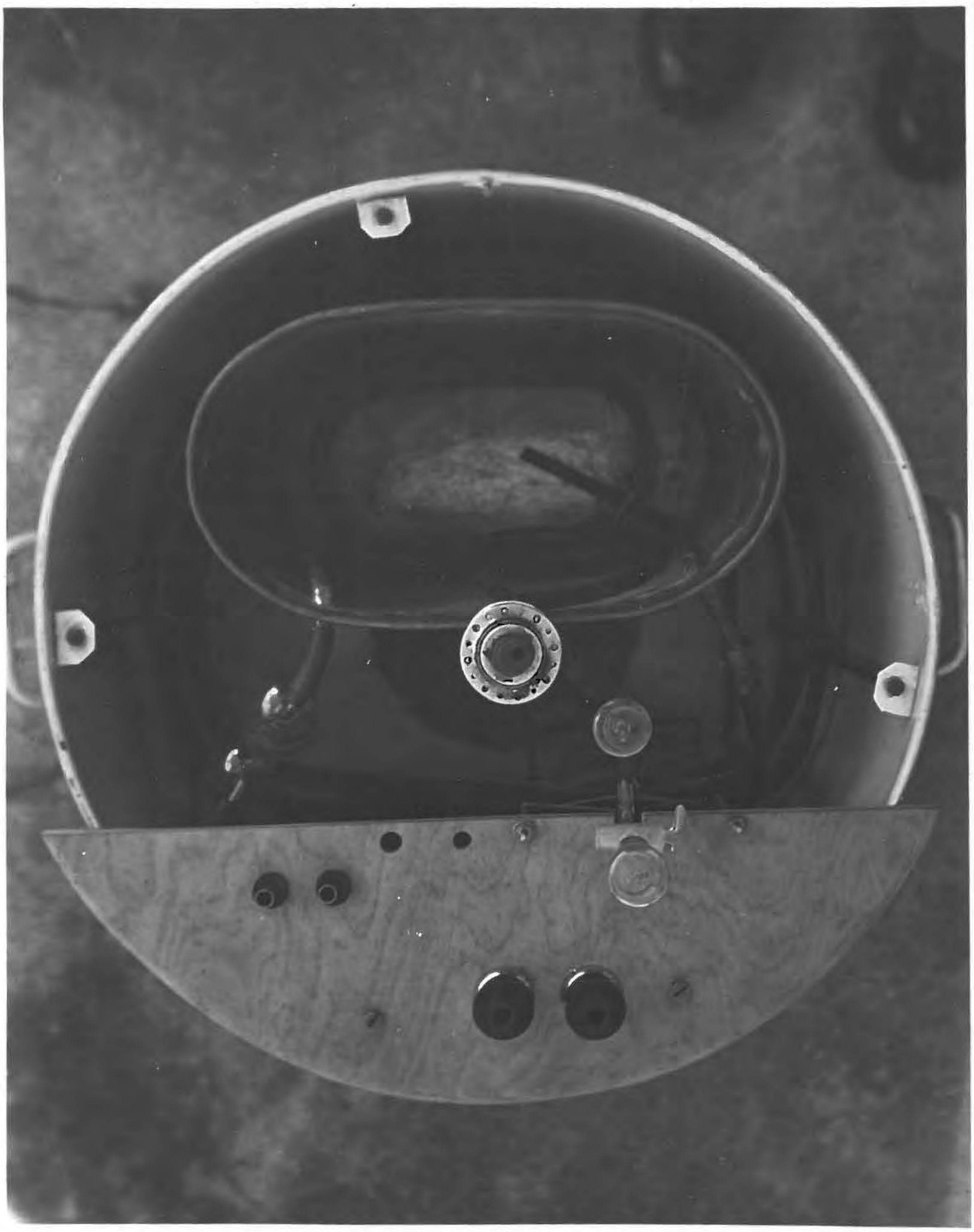


PLATE XI

The maximum variation in the temperature of the outer vessel is 0.003°C. The variation in the inner vessel will probably be less than this, and that in the cell even less.

(ii) The Cell.

It is clear from the literature that a big proportion of the cells, used in conductometric work, have suffered from certain electrical defects, notably the Parker Effect, and this has made them unsuitable for accurate work. The Parker Effect may be described as the provision of an alternative path to the A.C. applied to the electrodes, as a result of the leads to the latter being in close proximity. The effect is especially pronounced when the lead tubes are of appreciable diameter, and filled with mercury. The net effect of this is that the measured resistance of the cell will be slightly lower than the true value.

Cells have recently been designed in which an effort has been made to reduce this Parker Effect by separating the lead tubes as much as possible. In the Gledhill cell, thin lead wires run down two relatively wide lead tubes, which are well separated. The lead tubes are thus separated from the outside liquid by an insulating column of air.

For the present work it was clear that, as precipitates of Cr $(OH)_3$ would be formed during titrations, a cell incorporating the dipping type electrodes would be preferable, to make for ease in cleaning the cell. The design finally decided upon is shown in Fig. XI. The lead tubes are ½" in diameter, and the lead wires are held in position by capillary tubing placed inside the lead tubes. To ensure that the electrodes are held rigidly in position, the two lead tubes are joined by a glass tube fairly close to the electrodes. In addition, the lead tubes fit tightly in the ebonite cover, and are fixed to the latter with de Khotinsky cement. The whole assembly is very rigid.

It was originally intended to construct the cell wholly of Pyrex glass, and the initial experiments were concerned with sealing Pyrex onto platinum tubes. After two weeks of unsuccessful attempts, these experiments were discontinued and the cell constructed of soda glass. The glass to platinum join was achieved by using cobalt glass. It should be pointed out that, in this case, there was no real disadvantage in using soda glass, as all titrations were to be carried out quickly. Furthermore, Festenstein (4) had found that pyrex is not very much more resistant to alkali attack than ordinary soda glass.

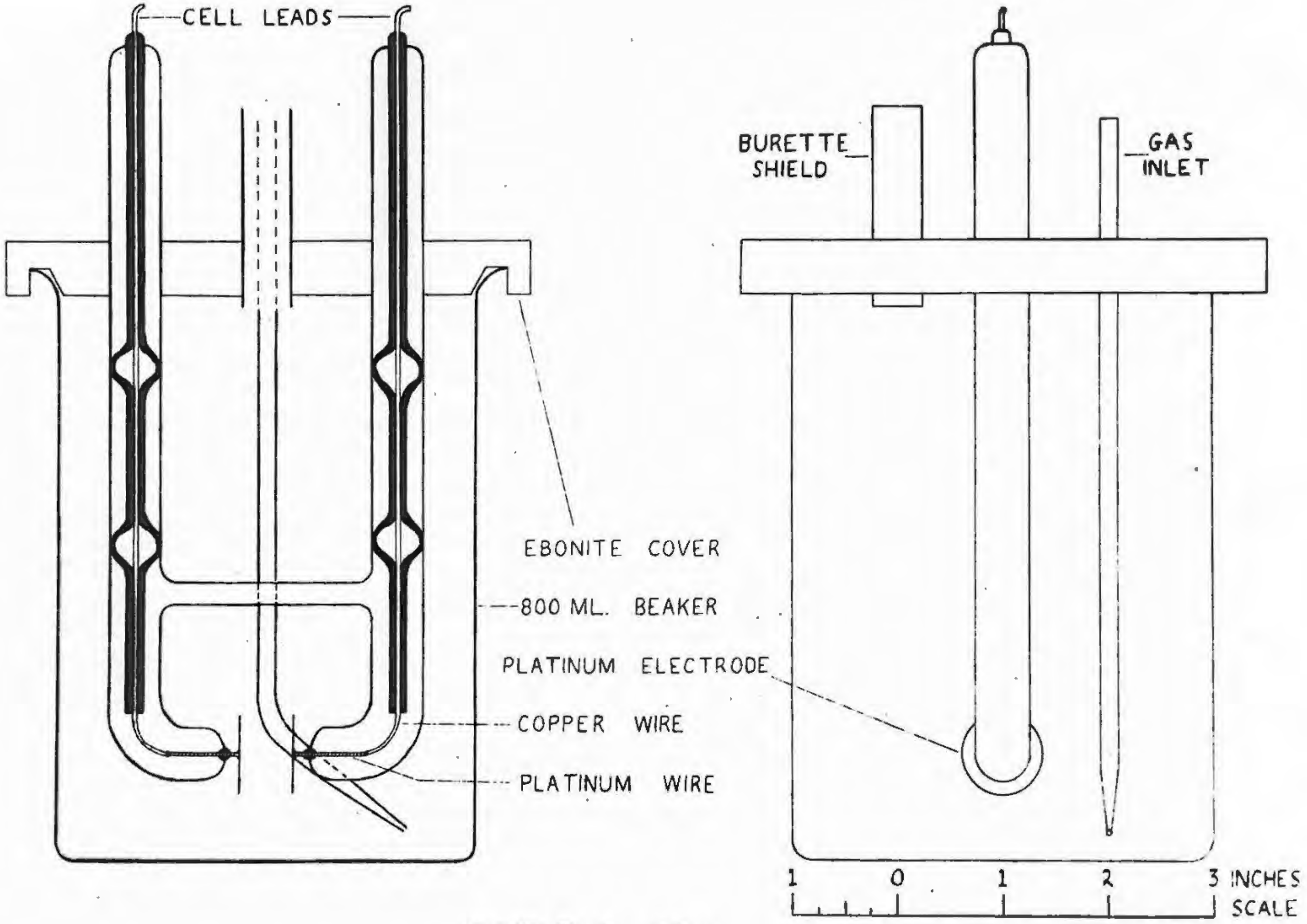


FIG. XI THE CELL

An innovation in the cell is the position of the gas stirrer tube, which directs the stream of bubbles away from the electrodes. Thus it was hoped to obviate the necessity of having to turn off the gas stirring when taking readings. Gledhill (loc. cit.) mentioned that each time a bubble passed the electrodes in his cell, the bridge became momentarily unbalanced. The effect on the present bridge would be to send the image off the oscilloscope screen, so making balance rather difficult. The effectiveness of this innovation is discussed later. Tests were carried out with coloured solutions to see if the stirring were efficient. At a rate of 4-6 bubbles per second, thorough mixing occurred in a few seconds.

The excess gas leaves the cell through the glass tube marked "burette shield". The nozzle of the burette is placed centrally within this tube so that its tip is just visible above the ebonite cover. With this device it is possible to ensure that the last drop of titrant always falls from the burette tip.

The resistance of the cell leads was determined by shorting out the electrodes with pure mercury, and was found to be only 0.05 ohms. However the leads from the bridge to the cell have a resistance of 0.35 ohms, so that 0.4 ohms must be subtracted from each reading taken on the bridge.

(iii) The Burette.

It has been customary in most conductometric work to add reagent to the cell from a micro-burette. Kolthoff (37) recommends that the reagent be at least twenty times as strong as the solution being titrated. If a volume correction is to be avoided, this factor is increased to at least 100, and even then, in very accurate work, a small correction has to be applied. Recently, however, certain workers e.g. Shuttleworth (38), Burton and Taylor (39), have used very weak solutions as titrant, and have employed macro-burettes for additions to the cell. It was decided to investigate the problem on theoretical grounds.

Errors in Applying a volume correction.

The "volume correction" is applied to the observed conductivity, $K_{obs.}$, by multiplying it by a factor $\frac{200 + x}{200}$, to allow for dilution, x being the number of ml. of titrant added to, say, 200 ml. of solution. The corrected conductivity, K_{corr}, is given by

$$K_{corr.} = K_{obs.} \cdot \frac{200 + x}{200} \qquad \text{— (1)}$$

Now consider the titration of an acid or salt of concentration C_o with water. After the addition of x ml., the concentration C_x is

$$C_x = C_o \cdot \frac{200}{200 + x} \qquad \text{— (2)}$$

For concentrations of C = 0.00 1N. or less, the conductivity is given by the Debye-Hückel - Onsager equation.

$$C = \Lambda_o - A\,C^{\frac{1}{2}}$$

$$\text{or}\quad K = \frac{\Lambda_o}{1000}.C - \frac{A}{1000}\,C^{3/2} \qquad -(3)$$

If K_o = specific conductivity at $x = 0$

$$K_o = \frac{\Lambda_o}{1000}.\,C_o - \frac{A}{1000}.\,C_o^{\;3/2} \qquad -(4)$$

When $\underline{x}$ ml. of water have been added, the specific conductivity is

$$K_{obs.} = \frac{\Lambda_o}{1000}.\left(\frac{200}{200+x}\right) C_o - \frac{A}{1000}\left(\frac{200}{200+x}\right)^{3/2}.\,C_o^{\;3/2}$$

from which, in terms of (1), we obtain

$$K\,corr. = \frac{\Lambda_o}{1000}.\,C_o - \frac{A}{1000}\left(\frac{200}{200+x}\right)^{\frac{1}{2}} C_o^{\;3/2} \qquad -(5)$$

Thus K corr. will be greater than Ko by an amount

$$\Delta K = K\,corr. - K_o = \frac{A}{1000}\left\{1 - \left(\frac{200}{200+x}\right)^{\frac{1}{2}}\right\} C_o^{\;3/2} \qquad -(6)$$

It seems clear, therefore, that it is only permissible to apply a proportionate volume correction in conductometric titrations where the values of ΔK are kept low, e.g. consider the titration of HCl. into water. The volume of $\frac{N}{200}$ HCl (being the normality employed by Shuttleworth (loc. cit.)) required to bring 200 ml. of water to $\frac{N}{1000}$ is 50 ml., whereas the volume of $\frac{N}{10}$ HCl. (the more usual strength employed) is only 2 ml. The corresponding values of ΔK are calculated as

$\Delta K(50) = 0.0051 \times 10^{-4}$

$\Delta K(2) = 0.0002 \times 10^{-4}$

Now $K_{HCl} \doteqdot 4 \times 10^{-4}$, for 0.001 N. solution

$\therefore$ the error introduced by using $\frac{N}{200}$ titrants works out at 0.125%, whilst that due to the $\frac{N}{10}$ titrant is much less. It is clear, therefore, that, if an accuracy of more than 0.125% is required, the use of $\frac{N}{200}$ is to be avoided.

Another factor to recommend the use of micro-burettes is that practically no wait is necessary after each small addition of titrant to the cell, to allow the latter to reach temperature equilibrium with the thermostat. This is rather important in work on chromic solutions, because the latter are subject to continuous changes in conductance with time, as will be shown later.

The microburette used has a capacity of 2 ml, and may be read to 0.001 ml. without any difficulty. It has a specially constructed tip, which makes for uniformity of the delivered drops. Attached to the graduated portion of the burette is a reservoir of capacity 25 ml. The burette may be refilled as desired.

Drainage errors, encountered during the calibration of the burette, indicated that cold chromic acid does not clean glass effectively, even over a period of 48 hours. These errors were eventually reduced to a minimum by filling the burette with ethanol, rubbing the bore gently with a thin glass rod, and then rinsing thoroughly with water.

Tests were carried out on a variety of burette greases, and it was found that none of them retained its efficiency after more than two titrations had been carried out. This was in spite of the fact that the burette taps had been meticulously ground. The effect was especially pronounced with alkaline solutions as titrants. In the absence of a better grease, a variety produced by Kahlbaum was used, and the burette was recleaned and regreased after every two titrations.

The burette, in position for a titration, may be seen in plate X.

(Note: Recently a highly satisfactory Silicone burette grease has been manufactured - this had been ordered by the Department but, unfortunately, did not arrive in time).

(iv) Pipettes.

All pipettes used in this work were accurately calibrated.

C. PREPARATION OF MATERIALS.

(i) Conductivity Water.

This was prepared by the method suggested by Mr. P.K.Faure, B.Sc., who will give a full description of it in his M.Sc. thesis. (In brief - distilled water, containing phosphoric acid to remove any dissolved ammonia, is distilled through a fractionating column and a condenser, and collected). The water was kept in well steamed-out Jena flasks, which had previously been thoroughly cleaned by the alcohol-nitric acid treatment. The flasks were closed with tin-foil covered rubber stoppers. Fresh water was prepared every day.

Values of the conductivity of the water are given later.

(ii) CO_2 - free Sodium Hydroxide.

Vogel (45) states : "If a concentrated solution of sodium hydroxide, containing equal weights of solid and water, is prepared and allowed to stand, the carbonate remains insoluble; the clear carbonate-free liquid may be poured or siphoned off, and suitably diluted". To hasten the process of carbonate separation, the concentrated NaOH solution was centrifuged; after a day the liquid was absolutely clear. The final dilution was made with freshly distilled conductivity water, and the solution kept in a waxed Pyrex flask, protected from contact with the atmosphere. Solution was withdrawn from the flask by applying a pressure of CO_2- free air to it which forced the liquid out of a thin delivery tube. In spite of this precaution, the Na OH was renewed every two weeks. Standardisations were carried out against standard H Cl and potassium hydrogen phthalate (in both cases in a CO_2- free atmosphere). The normality of the different Na OH solutions was adjusted to the same value throughout.

(iii) Hydrochloric Acid.

The hydrochloric acid used was prepared by dilution of constant boiling point hydrochloric acid. It was standardised against borax, which had been twice recrystallised and kept over saturated sugar - salt solution. The standardisation was done three times over a three month period, and the normality found to have remained constant.

(iv) Potassium Chloride.

Kahlbaum's G.R. KCl was recrystallised twice, and then fused in a platinum crucible, as directed by Jones and Bradshaw (40).

(v) Chrome Alum.

The sample used was Riedel de Haën A.R. crome alum. It was purposely not recrystallised.

(vi) Air for Stirring.

The air used for stirring the contents of the cell was passed from the compressor tap through a long train of soda lime tubes (to remove CO_2), and then through two sulphuric acid bottles (to remove ammonia, and to dry the air somewhat). It was then passed through two bottles containing distilled water (which saturates it with water vapour at 24°C.) and then into the thermostat where it is brought to 25°C. Before finally reaching the cell it passes through a potash bulb filled with distilled water at 25°C., so as to saturate it finally with water vapour at that temperature.

B. EXPERIMENTAL SECTION.

It is a well-known fact that the chromic sulphate salts (both the violet and green varieties) tend to degenerate into pasty masses; in addition, there appears to be some doubt as to the number of attached water molecules. For these reasons, it was decided to use chrome alum (at least for the initial experiments) as it forms a stable hydrate at ordinary temperatures. It dissolves in water to give the normal violet solution; on boiling these solutions they are converted to the green.

Technique.

The initial cleaning of the cell presented some difficulty. As it was constructed of soda glass, any method involving the use of hot or boiling solutions had to be avoided, for fear of cracking the glass. The possibility of cleaning the cell with chromic acid was considered. Morgan and Lammert (41), however, deprecated this procedure as they stated that it damages the platinum.

The glass portions were eventually cleaned with alcohol and a soft cloth. The electrodes were cleaned in a deplatinising HCl - H_2O_2 mixture. The cell was then immersed in conductivity water for a day, during which time the water was changed twice. In this way as much as possible of any substance adsorbed by the platinum or the glass was removed.

After this the cell was rinsed again and drained completely; it was never dried, as this injures the electrodes, especially if these are platinised. 400 ml. of conductivity water were pipetted into the cell, the assembly placed in the thermostat, and the air stirring turned on.

After each titration the cell was immediately rinsed out and then filled with dilute H Cl to remove any precipitated Cr $(OH)_3$. After an hour the HCl was replaced by conductivity water. Before each titration the cell was rinsed four times with distilled water and six times with conductivity water.

Experiment 1.

300 ml. of conductivity water were pipetted into the cell, and resistance readings commenced. As the resistance of the water was well in excess of 100,000 ohms, it could not be read directly on the bridge. For this reason, a 10,000 ohm resistance was placed in parallel with the cell (as suggested by Shedlovsky (42)). The image on the oscilloscope screen was very unsteady, and this was correctly ascribed to the amount of water in the cell being insufficient to keep the electrodes permanently immersed. Accordingly, another 100 ml. was pipetted into the cell and this appeared to check the fault. If, however, the gain of the amplifier were turned right up, the effect of the bubbling could

still be noticed, but balance to 1 part in 10,000 was easily attainable. Had a greater precision than this been required, it would have been necessary to switch off the stirring when taking readings.

With the comparatively fast rate of bubbling employed, it was found that the resistance of the water rose to a steady value in just over an hour, and then proceeded to fall slowly. The maximum value obtained was noted and then the resistance of the 10,000 ohm resistor measured. Using an approximate value of the cell constant of 0.156 (which had been roughly determined before), the specific conductivity of the water was calculated as 6.3×10^{-7} . This value is recomputed more accurately later.

Experiment 2.

This was to determine the cell constant by measuring the conductance of a standard KCl solution. A 0.01D. solution was prepared according to the directions of Jones and Bradshaw (40). The specific conductivity of the KCl is 0.0014088 at 25°C., and to this must be added the specific conductivity contributed by the water.

The cell was rinsed out six times with the solution before filling, so that any adsorption would take place during the initial washings.

The resistance of the solution was in the neighbourhood of 110 ohms, and balance of the bridge (especially at the low frequency end) proved to be extremely difficult because of the high parallel capacity required. For this reason a wire wound resistance, R_s, of value approximately 1300 ohms, was placed in series with the cell and the total resistance determined; the value of R_s was also measured, and hence the cell resistance obtained by subtraction. In both determinations one coil of the 1000 ohm decade was used to obtain balance, so that any error in this coil would be cancelled or subtraction. Both Gledhill (3) and Festenstein (4) used a value of R_s slightly less than 1000 ohms, and therefore had to take the maximum possible error in the 1000 ohm coil into consideration, as the combined resistance of R_s and R_{cell} exceeded 1000 ohms.

The final resistance readings were taken when a constant value had been reached: this again took just over an hour. The corrected values of the cell resistance, R, at the different frequencies, f, are tabulated below.

f (C.p.S.)	R (ohms)	$f^{-\frac{1}{2}}$
2000	113·02	·02236
1300	114·13	·02768
900	115·38	·03333
650	116·83	·03924
500	118·28	·04472

The values of $(C_3 - C_4)$ required for balance were, in all cases, too small to make the term $p^2C^2R^2$ appreciable. In fact, at no time during the work was it necessary to take this term into account.

The great difference in resistance readings at the five frequencies is apparent from the tabulation. There is a discrepancy between extreme values of as much as 5%! In order to determine the polarisation correction, and hence the true cell resistance, R was plotted against $p^{-\frac{1}{2}}$ (See Fig. XII) according to the method of Jones and Christian (20). It is clear from the figure that the points lie on some form of curve, and it would be a matter of some difficulty to decide where the curve cuts the Y axis. If it is assumed that this happens at ±110 ohms, it is clear that errors of as much as 9% are possible when working at one fixed frequency. This immediately throws suspicion onto work where bright platinum electrodes are employed, and especially that carried out at only one frequency of operation. It is also clear that, under the conditions of the previous experiment, the Jones-Christian method does not allow the true resistance of the cell to be computed easily.

The most effective way of cutting down the polarisation of a cell is to platinise the electrodes. Jones and Bollinger (43) found that the first small amounts of

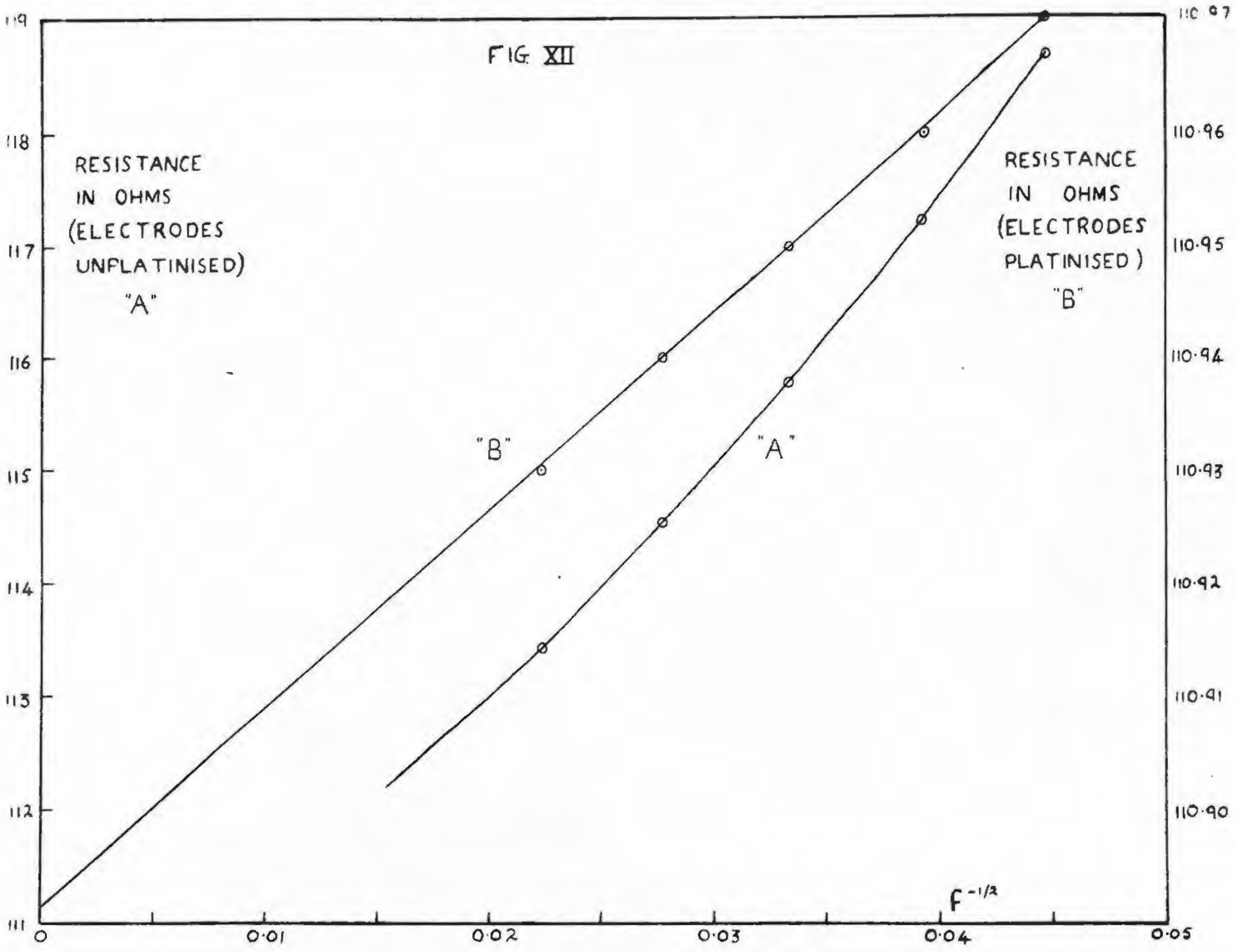


FIG XII

RESISTANCE IN OHMS (ELECTRODES UNPLATINISED) "A"
RESISTANCE IN OHMS (ELECTRODES PLATINISED) "B"
"A"
"B"
$F^{-1/2}$
111
112
113
114
115
116
117
118
119
110·90
110·91
110·92
110·93
110·94
110·95
110·96
110·97
0
0·01
0·02
0·03
0·04
0·05

platinum deposited resulted in a very marked decrease in the reactance of the cell and the polarisation, but that further amounts of platinum had less and less effect. The reactance of the cell could be reduced to a minute value if the electrodes were heavily platinised, but this is inadvisable because of the attendant dangers of adsorption. Accordingly, the electrodes were given a very light and slow platinisation (12 coulombs each, by passing a current of 0·01 amperes for 40 minutes). After this treatment the cell was again immersed in conductivity water for a day, and the water changed periodically.

The cell was then filled with 0·01 D. KCl solution, and resistance readings taken. It was immediately apparent that the reactance of the cell had decreased very appreciably, but it was still a matter of difficulty to balance the bridge on the low frequencies because of the large values of additional capacitance required. As before, the 1300 ohm resistance was placed in series with the cell. The values of the cell resistance are tabulated below.

f (c.p.s.)	R (ohms)
2000	110·93
1300	110·94
900	110·95
650	110·96
500	110·97

The improvement over the previous values is very striking - the maximum variation in resistance has been reduced from 5% to 0·04% ! In addition, the points on the R vs. $f^{-\frac{1}{2}}$ graph lie quite well on a straight line, giving 110·89 ohms as the true resistance of the cell.

The conductivity of 0·01 KCl = 0·0014088, and assuming the conductivity of the water is $6 \cdot 3 \times 10^{-7}$ gives the conductivity of the solution as 0·0014094

$\therefore$ Cell constant = 0·0014094 x 110·89

= 0·1562(5

Resubstituting this value of cell constant did not alter appreciably the value obtained for the conductivity of the water, and therefore 0·1563 was taken as the constant of the cell.

Experiment 3.

As speed was obviously an important factor in this work, it was decided to use only one frequency (1300 c.p.s.) of operation.

In this experiment preliminary titrations of NaOH into unboiled solutions of Chrome alum were carried out. An amount of Chromium equivalent to approximately 6 ml. NaOH was required; therefore 0·1000 gm. Chrome alum was dissolved in 400 ml. water, which had been temperature equilibrated for an hour. The titration was carried out as fast as possible, and a graph of conductance vs. volume NaOH was plotted. It was found that straight lines could be drawn through the different points obtained (See, e.g., Fig. XIV), but not with absolute certainty. Shuttleworth (38), on the other hand, obtained a series of four distinct straight lines. A second titration, carried out in 30 minutes, yielded the same results as before.

At this stage, the points of difference between the set-up of the author and that of Shuttleworth were considered with a view to ascertaining if these were capable of explaining the difference in results. These considerations suggested that the factor, most likely to be responsible, was the difference in electrodes. In the Shuttleworth cell the electrodes were not platinised; furthermore the cell was probably subject to considerable Parker Effect, as the lead tubes were close together and were filled with mercury.

Experiment 4.

In order to examine the effects of polarisation, adsorption, and Parker Effect on the accuracy of an ordinary conductometric titration, tests were carried out on three different cells.

(a) the cell used up to the present. The electrodes had been platinised, and the cell was therefore subject to very small polarisation errors. There was little likelihood of Parker Effect, but there was a possibility of adsorption.

(b) a cell similar in construction to the last, but with electrodes unplatinised. The cell was subject to little adsorption and Parker Effect, but polarisation errors were to be expected.

(c) a cell similar in construction to that of Shuttleworth. There was little probability of adsorption, but considerable likelihood of Parker Effect and polarisation errors.

To start with, the cell constants of (b) and (c) were determined using 0·01 D.KCl.

f(c.p.s.)	$R(A_o)$ in ohms	R(a)	R(b)	R(c)
2000	113·02	110·93	122·01	179·15
1300	114·13	110·94	122·49	180·48
900	115·38	110·95	123·04	182·14
650	116·83	110·96	123·78	184·49
500	118·28	110·97	124·52	186·45

The first column of the above table refers to the values obtained using cell (a) before the electrodes had been platinised. There is much less variation in the resistance values, R(b) than in the values $R(A_o)$ or R(c). This was ascribed to the fact that the

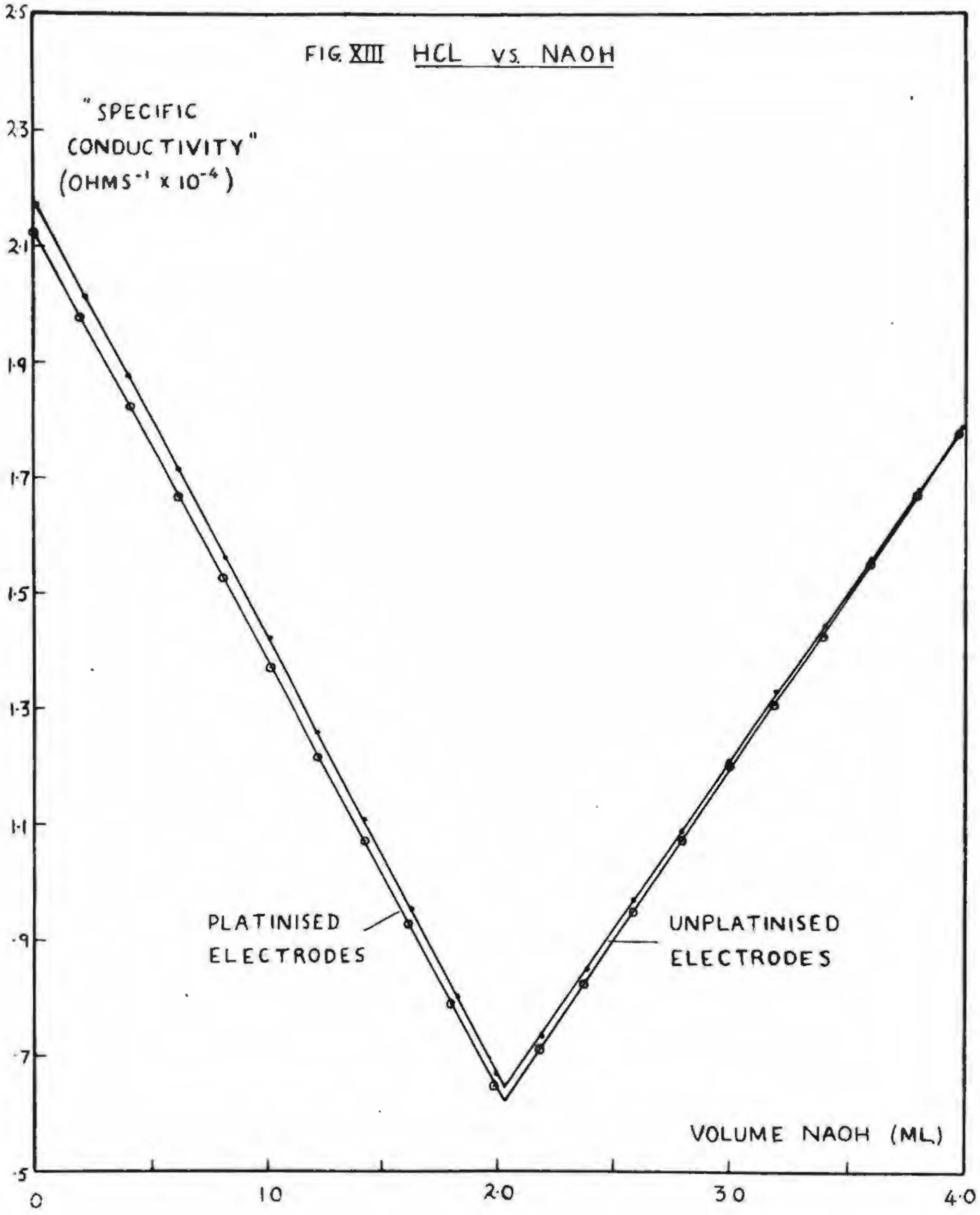


FIG. XIII HCL vs. NAOH

initially bright electrodes of cell (b) had been badly scratched during the welding onto them of the platinum leads. For this reason, they had been repolished on a very fine abrasive paper. This treatment, however, must have increased the effective surface area of the platinum and hence decreased the extent of polarisation (an effect similar to depositing a thin layer of platinum black on the surface). Another point which emerged was that the capacity, C, required for obtaining balance in cell (c) was very much larger than the values previously encountered.

As all future measurements were to be taken at 1300 c.p.s., the "cell constants" of the cells were worked out at this frequency. Only in the case of cell (a) would the "cell constant" be effectively equal to the true cell constant.

Experiment 5.

A conductometric titration of Na OH into HCl was carried out using each of the three cells. 2 ml. of± 0·1N HCl was pipetted into 400 ml. conductivity water and then titrated with the standard NA OH. This high dilution was used in order to promote the effects of adsorption, if any.

Two of the graphs obtained (Cell (a) and Cell (c)) are shown in Fig. XIII; the graph obtained with cell (b) was too similar to that obtained with Cell (a) to be conveniently plotted on the same graph. The end-points obtained agreed with each other to within 1 part in 400. It appears, then, that, although the slopes of the graphs are different, the end-points obtained are virtually the same, which indicates that :

i) adsorption errors, if present, are only very slight.

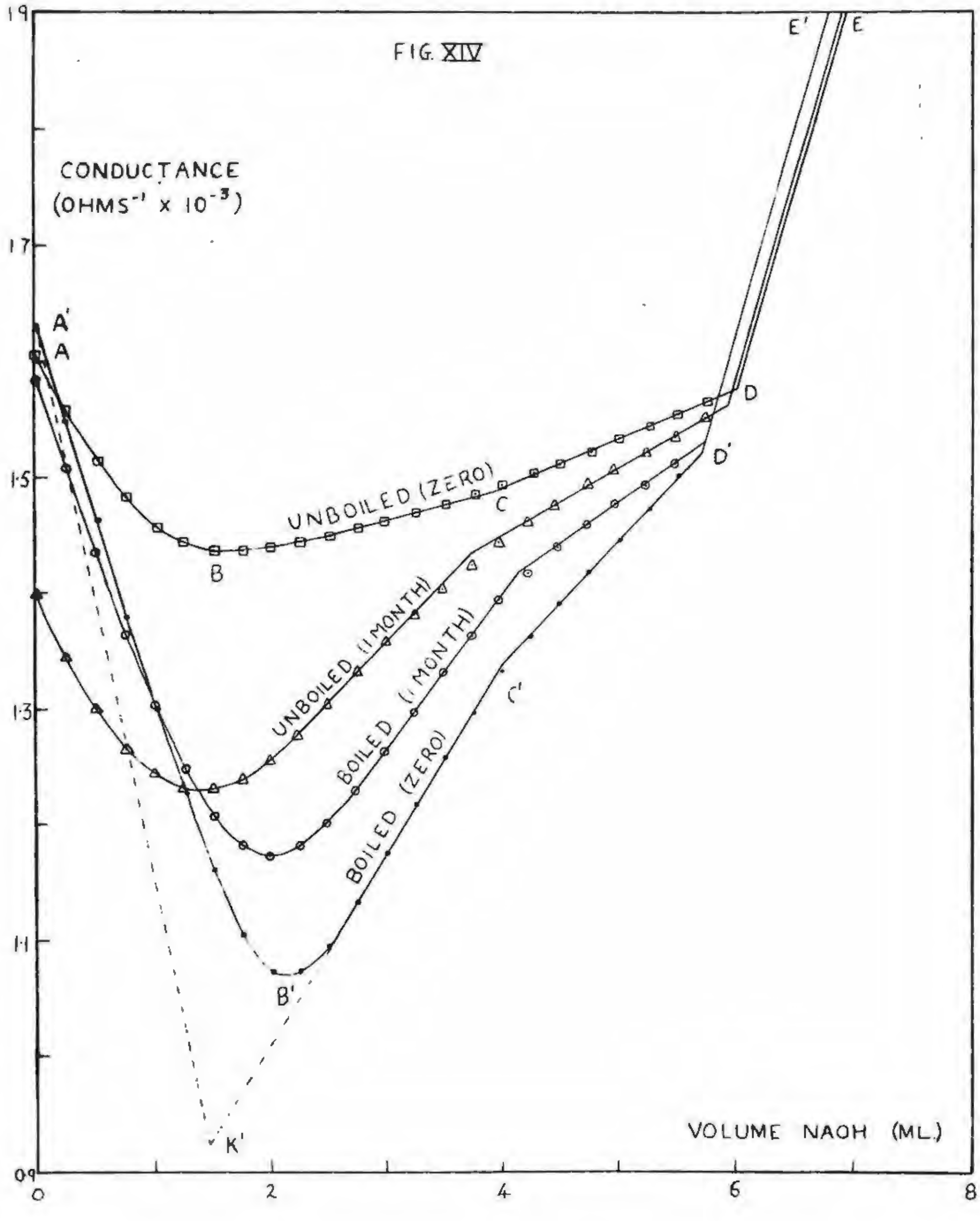
ii) although polarisation results in the individual resistance readings being incorrect, the actual end-point is not appreciably altered.

iii) the Parker Effect increases the capacitance necessary for balance.

As a further check, a titration of Na OH into an unboiled Chrome alum solution was carried out using the Shuttleworth cell. It was much more difficult to obtain balance because of the large values of additional capacity necessary, and because of the fact that the stirring had to be switched off when taking readings. The graph obtained was essentially the same as that obtained before with Cell (a).

(Note: It was found later that Shuttleworth (44) had performed further experiments in which he, too, obtained this type of graph. He justified his previous work by stating that the type of graph obtained was dependent on the method of manufacture of the Chrome Alum).

FIG. XIV



CONDUCTANCE
(OHMS⁻¹ x 10⁻³)
1·9
1·7
1·5
1·3
1·1
0·9
0
2
4
6
8
VOLUME NAOH (ML.)
UNBOILED (ZERO)
UNBOILED (1 MONTH)
BOILED (1 MONTH)
BOILED (ZERO)
A'
A
B
B'
C
C'
D
D'
E'
E
K'

Experiment 6.

A series of titrations was carried out on unboiled and boiled chrome alum solutions, until the time per manipulation had been reduced to 20 - 25 minutes. The unboiled solutions were made by diluting 10 ml. of a 10 gm. / litre chrome alum solution to 410 ml.; the solutions for boiling also contained 10 gm. / litre, and were boiled for 30 minutes, rapidly cooled and then made to the required volume. As before, 10 ml. of the boiled solution was diluted to 410 ml.
(Note: (i) Atkin and Chollet (23) proved conclusively that the nature of the solution, obtained by boiling, is dependent on the initial concentration of that solution. For this reason, the initial concentration of these solutions was always made the same.

(ii) Burton and Taylor (39) showed that boiling for any length of time between 10 minutes and 3 hours makes no difference to the final solution.)

The types of graph obtained may be seen in Figs. XIV, XV, and XVI. Each of the graphs may be divided into four sections :

(i) an initial big drop in conductance due, presumably, to the neutralisation of the strong acid produced by the hydrolysis of the chromic sulphate. This hydrolysis gives rise to the formation of a basic salt and free H_2SO_4. It is clear from the graphs that the boiled solutions are much more strongly acidic than the unboiled.

(ii) a rise in conductance during which the $\frac{1}{3}$ basic chromium sulphate is being converted to $\frac{2}{3}$ basicity.

(iii) a rise in conductance when chromium hydroxide starts to precipitate.

(iv) an abrupt rise in conductance due to excess Na OH.

Because of the increased hydrolysis effects in the vicinity of the end-points, it was a matter of some difficulty to fix the positions of the straight lines exactly, and so the points of inflection could not be obtained with great accuracy. The effect is especially pronounced in the case of the first equivalence point; as the free acid in solution is neutralised by the added Na OH, the equilibrium of the solution is upset and further hydrolysis occurs with the liberation of more free acid. This would appear to be contrary to the statement of Atkin and Chollet (23) to the effect that, because of the olation of the basic chrome sulphate, the free acid in solution is not in hydrolytic equilibrium with the basic salt.

Because of the very considerable hydrolysis that occurs during the early stages of the titration it is clear that the line <u>AB</u> will have quite the wrong slope. Shuttleworth (loc. cit.) has therefore proposed a method for determining the free acid initially present in solution, in which a line AK is drawn with a slope corresponding to the neutralisation of strong acid with Na OH (See Fig. XIV). The amount of free acid in solution is then given by the point of intersection of this line with the line BC. For the freshly prepared unboiled and boiled solutions the amount of free acid works out as equivalent to 0.45 and 1.45 ml. of the $\frac{N}{10}$ Na OH respectively. (The method proposed by Whitney (loc. cit.), in which the minima are taken as a measure of the strong acid, indicates values of 1·65 and 2·15 ml. Na OH respectively. It would appear that the Shuttleworth method gives the more likely results, an observation which is confirmed by a different method given later).

It will be noticed from the graphs that the slopes of BC and CD are much greater in the boiled solutions than in the unboiled. This is due to the fact that, in the former case, most of the SO_4 groups being attacked are inside the chromium complex (where they do not contribute to the conductivity of the solution), and during attack, they are transferred to the solution; in the latter case they are mainly electrovalent, and so contribute to the conductivity even before attack.

It is clear from the graphs that, although the solutions contain the same amount of chromium, the excess NaOH line starts sooner in the case of the boiled solutions. A calculation showed the amount of chromium

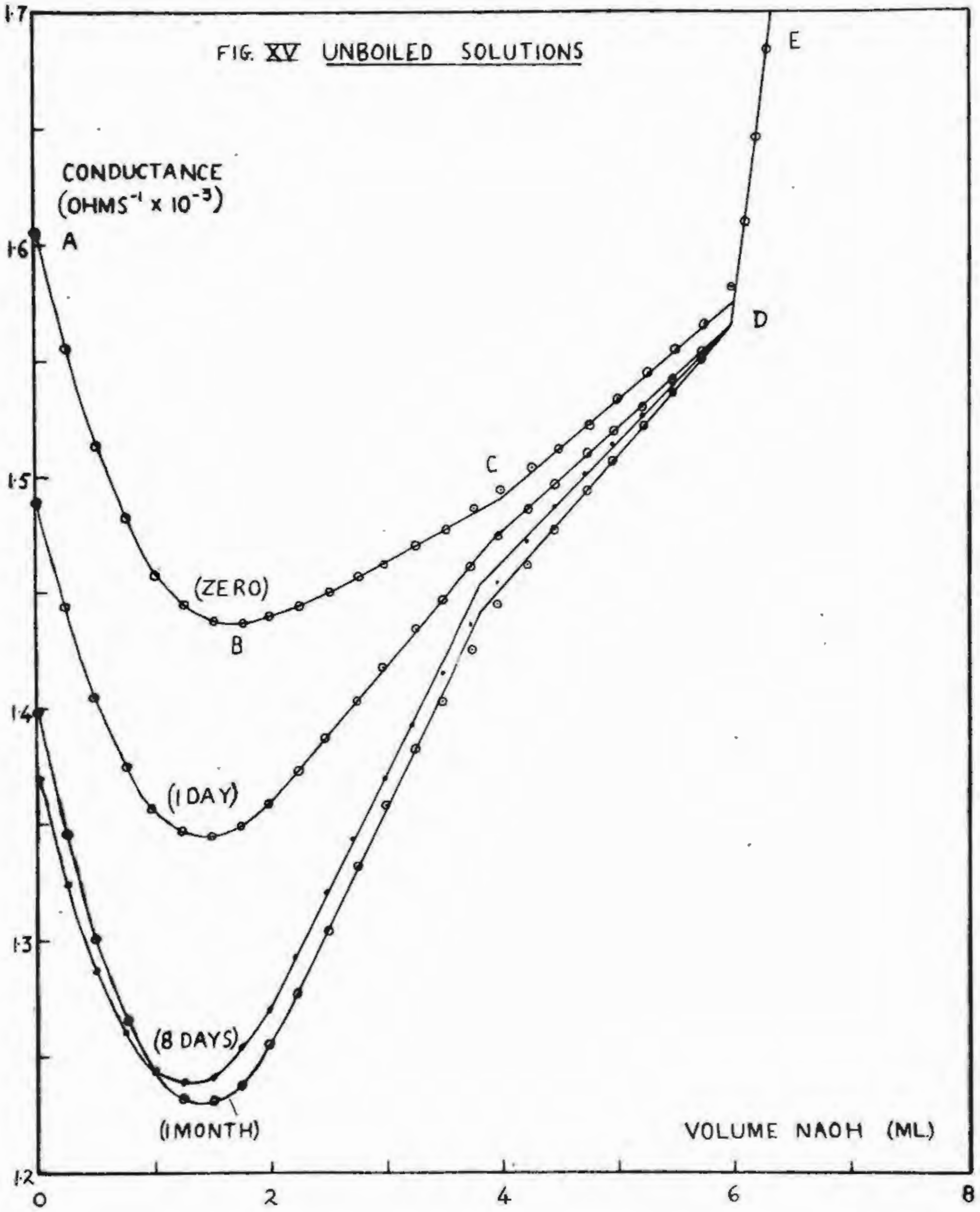


FIG. XV UNBOILED SOLUTIONS

present to be equivalent to 6·01 ml of the Na OH solution. In the case of the boiled solution, the excess NaOH line starts when only 5·70 ml. NaOH have been added.

Another very interesting point is that the conductances of the boiled and unboiled solutions are initially nearly equal.

In order to study the behaviour of the solutions during titration, some of these manipulations were carried out with the cell out of the thermostat. In the unboiled solution, precipitation became apparent after 3 ml. NaOH had been added, and the precipitate at the end was finely dispersed, giving the solution a milky appearance. In the boiled, precipitation appeared to start much later (4 ml NaOH), and the precipitate was of the more usual ~~heavey~~ heavy, gelatinous type which settled out quickly.

Experiment 7.

This was designed to investigate the statement of Miss Graham (28) and others that the green and violet solutions eventually reach the same equilibrium solution on ageing. The 10 gm/litre solutions were aged at 24°C. for the following periods :

1 hour, 4 hours, 1 day, 8 days, 1 month.

The titrations were carried out in duplicate, or repeated until the results obtained were in reasonable agreement with each other. Some of the graphs obtained may be seen in Figs. XIV, XV, and XVI, and some of the results obtained seen in the table below. (For clarity in Figs. XV and XVI, only the excess NaOH lines for the Fresh solutions are shown).

Boiled Solutions

Age	Initial Cond'ce x 10^4	Str. acid (ml. NaOH)	Final End-pt. (ml. NaOH)
Zero	16·30	1.48	5·70
1 hour	16·32	1·47	5·70
4 hours	16·35	1·45	5·70
1 day	16·68	1.43	5·70
8 days	16·29	1·32	5·76
30 days	15·84	1·18	5·78

Unboiled Solutions

Age	Initial Cond'ce x 10^4	Str. acid (ml. NaOH)	Final End-pt. (ml. NaOH).
Zero	16·06	0·43	6·02
1 hour	16·01	0·45	6·02
4 hours	15·90	0·48	6·02
1 day	14·89	0·50	5·98
8 days	13·70	0·55	5·96
30 days	13.98	0.63	5.95

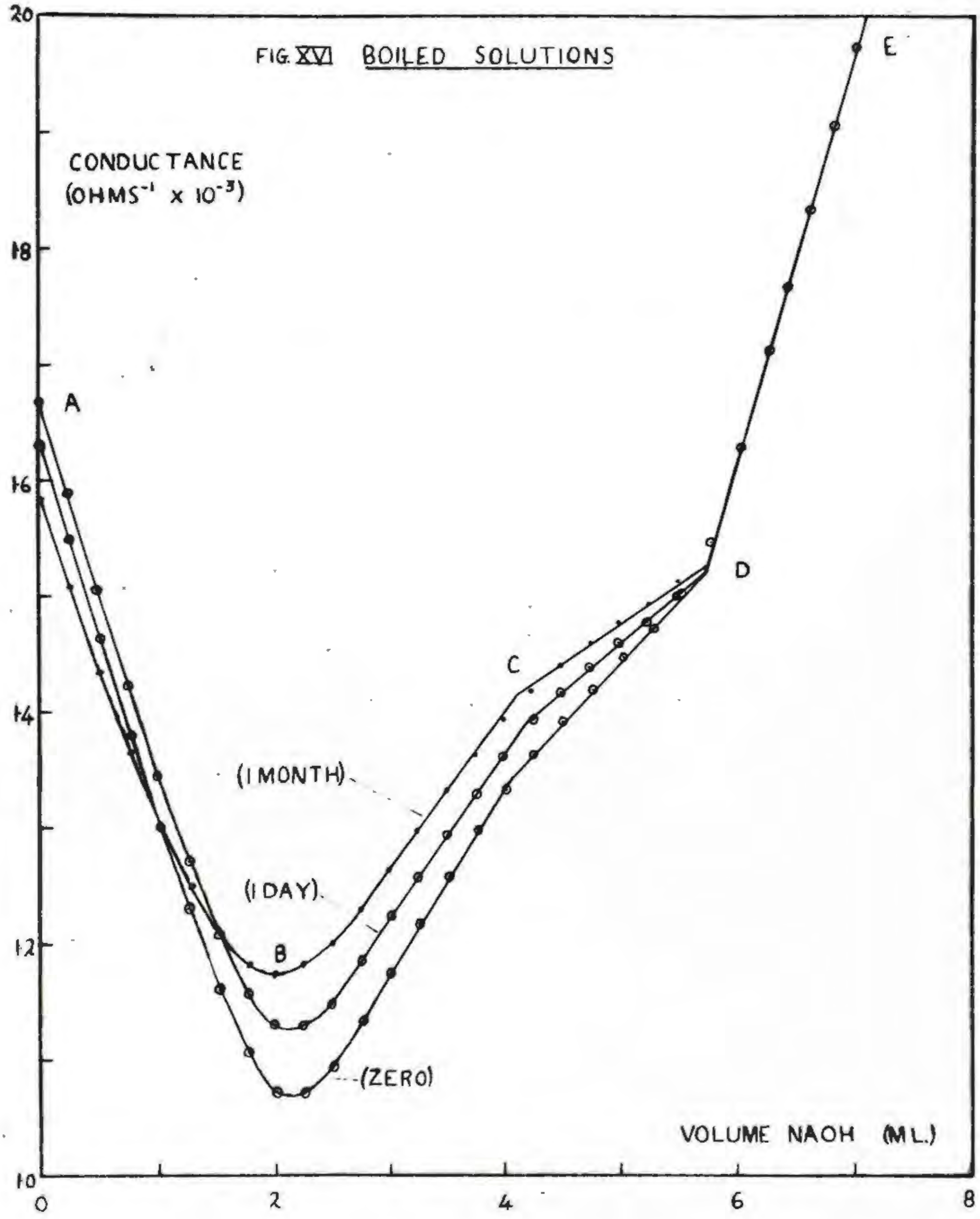


FIG. XVI BOILED SOLUTIONS
CONDUCTANCE
(OHMS⁻¹ x 10⁻³)
20
18
16
14
12
10
0
2
4
6
8
VOLUME NAOH (ML.)
A
B
C
D
E
(1 MONTH)
(1 DAY)
(ZERO)

The initial conductance of the unboiled solutions drops steadily with time, but eventually starts to rise again. That of the boiled rises slowly, and after 1 day starts to fall again. At the same time, the strong acid content of the unboiled solutions increases, and that of the boiled decreases, which bears out the observation of Richards and Bonnet (25). In addition, the final equivalence points of the solutions appear to be approaching one another. It is also clear from the graphs that, as the solutions age, the slopes of BC and CD increase in the case of the unboiled solutions, and decrease in the case of the boiled.

At the end of a month, the two solutions appeared to be almost identical in colour - emerald green, with a suggestion of violet when viewed into a source of light. It is, however, clear from the results that the changes were far from being complete.

At this stage, it was deemed advisable to attempt some other methods of investigation in an endeavour to throw some light on the problem.

Experiment 8.

To find out something of the nature of the sulphate radicles attached to the Chromium complex, titrations of 0·1N $BaCl_2$ into the unboiled and boiled solutions were carried out, using the same concentrations as before.

These titrations, however, proved to be of very little use, as the conductance of the solutions, after each addition of $BaCl_2$, varied so greatly that it was almost impossible to take readings of the resistance. Evidently the removal of sulphate ions from the complex upsets the equilibrium of the solution completely; Atkin and Chollet (23) deprecated the use of $BaCl_2$ to estimate the electrovalent sulphate (by gravimetric means), as they claimed that $BaSO_4$ is so insoluble that even coordinately linked SO_4 groups are withdrawn. This effect could probably be counteracted to a certain extent if the estimation were carried out at low temperatures (as was done by Law (34), during titrations of $AgNO_3$ into chrome chloride solutions), but as it was the intention to investigate the solutions at 25°C., this was not attempted.

The curves obtained for both green and violet solutions were as follows :
there was a sharp rise in conductance until a point, corresponding to the precipitation of one quarter of the sulphate present, was reached (due, probably, to the sulphate of the K_2SO_4 being precipitated); thereafter, the conductance rose less sharply to a point corresponding to the precipitation of all the sulphate present, after which the line for excess $BaCl_2$ was obtained. It was clear that the shapes of the graphs were greatly dependent

on the speed of manipulation. Further titrations were carried out, and a pause observed after each addition of $BaCl_2$ to see if the resistance of the solution would become steady. This, however, did not occur, and further titrations were abandoned.

Experiment 9.

It was felt that a pH study of the solutions during the titration with NaOH would be very useful. Accordingly, potentiometric titrations of the solutions were carried out at 24°C. Obviously it was necessary to use larger concentrations in this case; 50 ml. of the 10 gm./litre solutions were diluted to 250 ml. (equivalent, therefore, to ±30 ml of the $\frac{N}{10}$ NaOH). The pH of the solution during titration was followed by means of a Beckmann pH meter.

The curves obtained are very interesting, especially their initial sections (See Fig. XVII). In the violet, there is an almost rectilinear change in pH, whereas in the green, the change is similar to that which occurs during the neutralisation of a strong acid. In view of this Atkin and Chollet (loc. cit.) suggested an empirical method of determining the strong acid content of the green solutions. They stated that the curve is identical with that obtained by titrating (with NaOH) a solution of H_2SO_4 and K_2SO_4 to a pH value of 3·3.

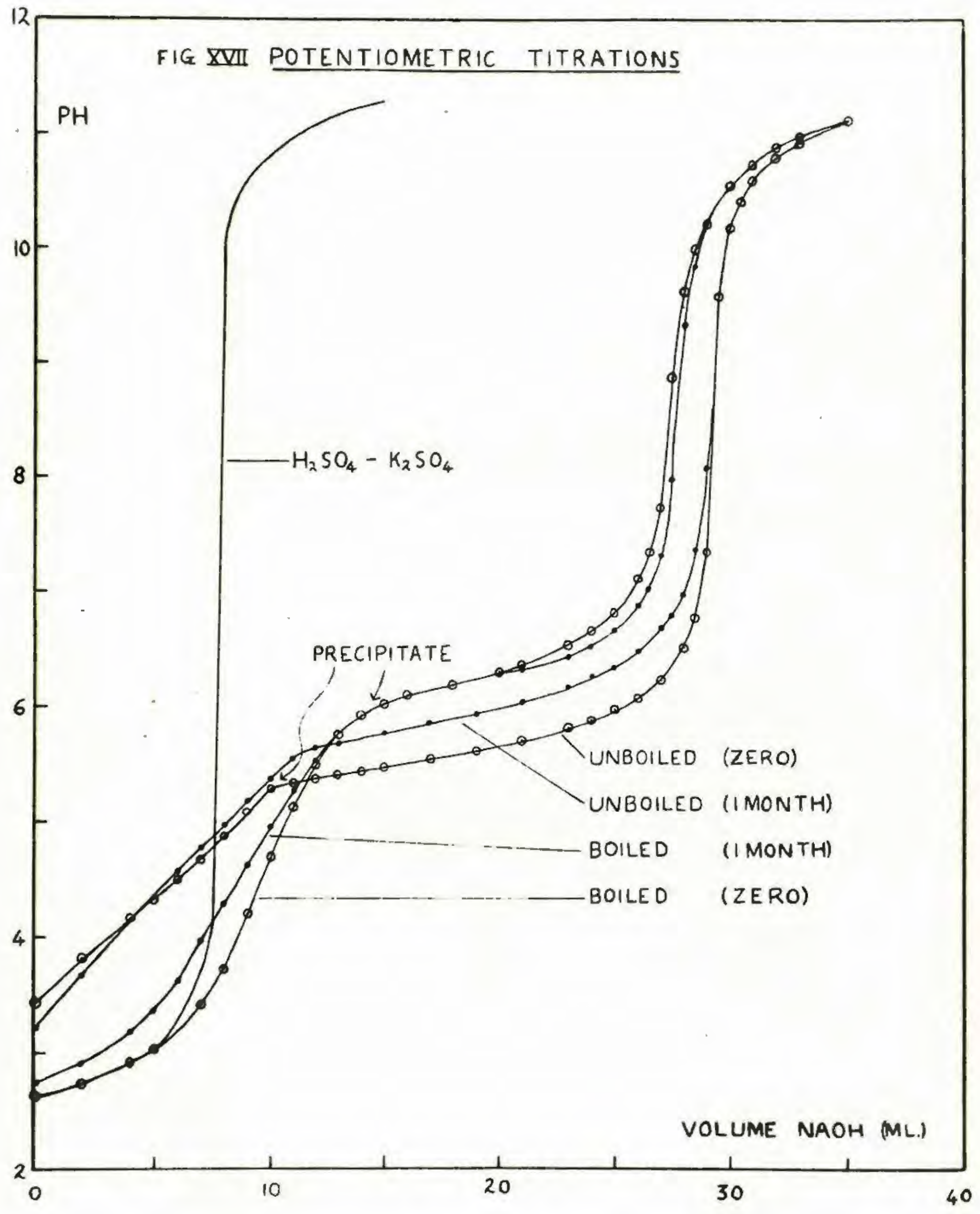


FIG XVII POTENTIOMETRIC TITRATIONS
PH
12
10
8
6
4
2
0
10
20
30
40
VOLUME NAOH (ML.)
$H_2SO_4 - K_2SO_4$
PRECIPITATE
UNBOILED (ZERO)
UNBOILED (1 MONTH)
BOILED (1 MONTH)
BOILED (ZERO)

After this point the curves diverge, and they took this point as a measure of the H_2SO_4 content of the solution.

This procedure was adopted, and a pH titration done on a solution of H_2SO_4 containing the correct amount of K_2SO_4. It is suggested that the H_2SO_4 content of the solution is given at the equivalence point of the test solution, and not at the point where the curves diverge. The value obtained is equal to 7·5 ml. of the $\frac{N}{10}$ NaOH; i.e. an amount of sulphate equivalent to one quarter of the total sulphate attached to the Cr atom is in the form of free acid. The agreement with the value obtained by the conductometric method of Shuttleworth is reasonably good (see later).

The appearance of a precipitate begins after the addition of ± 10 ml in the case of the unboiled and ± 15 ml in the case of the boiled solution. During precipitation the curves become very flat i.e. the pH change is small. As in the conductometric investigation, it is clear that final precipitation occurs earlier in the case of the green than the violet (27·5 and 29·3 ml NaOH respectively).

The difference in appearance of the precipitates is more marked in the more concentrated solutions. The boiled solutions give rise to a heavy, gelatinous turquoise-coloured precipitate which settles quickly, leaving a clear solution. The unboiled solutions give an olive-green precipitate which remains in suspension for several days.

pH titrations were also carried out on solutions which had been aged for 1 day, 8 days and 30 days. It is clear from Fig. XVII that, on ageing, the violet and green solutions become more similar to one another. The initial pH values of the two solutions, and their final end-points, appear to be approaching equilibrium values. The former are listed below:

	Zero	1 day	8 days	30 days
pH(Unboiled)	3·43	3·43	3·35	3·22
pH(Boiled)	2·64	2·64	2·70	2·75

It would appear from the graphs that the change in the solutions is just less than half way to completion after 1 month's ageing.

Experiment 10.

In this, the last experiment carried out, the change of conductance with time of the solutions was studied at the point A, and at a point on each of AB, BC, and CD, (See Fig. XIV) with a view to obtaining information about the solutions at the different stages during the NaOH titration. Lamb and Fonda (31) had applied this method to evaluating the hydrolysis constants of violet and green chromic chlorides by studying the changes in conductance of the solutions immediately after the salts had been dissolved.

The changes in the initial resistance values of the solutions with time may be seen from the following table:

Time	Boiled Solution	Unboiled Solution
0	620 ohms	623·00 ohms
1 mins	607·3	623·40
2	603.7	623.50
3	600.7	623·65
4	598·8	623·80
5	595·8	623.90
10	591·9	624·40
20	589·0	625·15
60	576·0	628.20
180	552·3	635.50

The decrease in conductance of the unboiled solutions is probably due to some electrovalent sulphate becoming coordinately linked. A slow increase in the conductance of the boiled solutions could be ascribed to an increase in the amount of electrovalent sulphate in solution, but the rapid increase in conductance can only be due to increased hydrolysis in the dilute solution, which increases the concentration of the highly mobile hydrogen ion. This again seems to indicate that there is hydrolytic equilibrium in solution and the evidence is therefore contrary to the statement of Atkin and Chollet (23) to the effect that, because of olation of the basic chromium salt, the free acid is not in hydrolytic equilibrium with the salt.

It was realised at this stage that, in order to have pursued this study effectively, it would have been essential to develop a type of cell in which the salt could be dissolved almost instantaneously, so as to allow conductance measurements to be taken immediately. Also, it would have been necessary to prepare pure samples of the violet and green sulphates.

It is suggested, however, that a comprehensive study of this type would be very informative.

E. DISCUSSION.

It is generally agreed that the violet and green chromic sulphates have the formulae

$$\left[Cr(H_2O)_6\right]^{+++}\ 3R^{-} \qquad \text{(violet)}$$

$$\left[Cr(H_2O)_4\ R_2\right]^{+}\ R^{-}\ .2H_2O \qquad \text{(green)}$$

in the pure salt form. (The slopes of the lines BC and CD in Figs. XIV, XV, and XVI indicate that there is much more electrovalent sulphate in the violet salt, which is in qualitative agreement with the formulae assigned). When either of these salts is dissolved in water, hydrolysis takes place with the liberation of free acid, until an equilibrium has been established. It is clear that this hydrolysis may (and probably does) take place in three stages, e.g. in the violet

$$\begin{aligned} \left\{\left[Cr(H_2O)_6\right]^{+++}\ 3R^{-}\right\} &\rightleftarrows \left\{\left[Cr(H_2O)_5\ OH\right]^{++}\ 2R^{-}\right\} + R^{-} + H^{+} \\ &\rightleftarrows \left[Cr(H_2O)_4(OH)_2\right]^{+}\ R^{-} + 2R^{-} + 2H^{+} \\ &\rightleftarrows \left[Cr(H_2O)_3(OH)_3\right] \qquad + 3R^{-} + 3H^{+} \end{aligned}$$

although the second and third hydrolyses probably occur to a much lesser extent than the first.

There is a further factor which complicates the system considerably : immediately upon solution of the violet and green salts, changes take place in the solutions, and these are complete only when the same equilibrium solution has been reached. e.g. If all the sulphate radicles were electrovalently linked in a solution of the violet salt (as the formula allocated to it suggests), section BC of the graph in Fig. XV would have a slope of almost zero. It is clear, however, that this is not the case. It is therefore likely that in solution there is present not only the ion $\left[Cr\ (H_2O)_6\right]^{+++}$ but also smaller amounts of $\left[Cr\ (H_2O)_5\ R\right]^{++}$ or $\left[Cr\ (H_2O)_4\ R_2\right]^{+}$, or possibly both. It is also clear that each of these ions is subject to a 3-stage hydrolysis, so this makes the consideration a highly complicated one. In the titration of the violet solution with NaOH, Shuttleworth (38) obtained zero slope for the line BC, showing that all the sulphate groups were electrovalently linked, and he found the amount of hydrolysed acid to be very small. In a later paper, Shuttleworth (44) obtained graphs in which BC had a definite slope, and which showed that there had been a marked increase in the amount of hydrolysed acid present. To account for this, he suggested that the method of preparation of the Chrome alum was the responsible factor.

It seems clear, then, that the unboiled solution consists mainly of the ion $\left[Cr\ (H_2O)_6\right]^{+++}$ with smaller amounts of one or both of the ions $\left[Cr\ (H_2O)_5\ R\right]^{++}$ and $\left[Cr\ (H_2O)_4\ R_2\right]^{+}$, whose hydrolyses contribute materially to the amount of free acid in solution.

The main constituent of the boiled solution is presumably $\left[Cr\ (H_2O)_4\ R_2\right]^+$, which appears to be very appreciably hydrolysed in solution. _If_ it is presumed that the green solution contains _only_ the above ion, the amount of free acid indicates that ≃ 75% of the ion is hydrolysed. It is, however, likely that there are smaller amounts of the other two ions in the boiled solution as well.

Another point which emerges is that, if $\left[Cr\ (H_2O)_6\right]^{+++}$ and $\left[Cr\ (H_2O)_4\ R_2\right]^+$ be considered the main constituent ions in the violet and green solutions, it would appear that the 2/3 basic violet salt is far less soluble than the corresponding green one, as is shown by the earlier formation of a precipitate in the case of the former. The fact that complete precipitation is achieved in the green solution before the stoicheometrical amount of hydroxide ions has been added suggests that a basic chromium sulphate is precipitated; i.e. that some of the coordinately linked sulphate is resistent to attack by NaOH under these conditions. This effect seems either to have been unnoticed or ignored by Shuttleworth (loc. cit.).

The experiments on ageing show clearly that the violet and green solutions tend to an equilibrium solution. In the violet solution, some of the electrovalent SO_4-- groups become coordinately linked and the amount of hydrolysed acid increases; in the green solution, there is an increase in the number of electrovalent sulphate radicles, and the amount of hydrolysed acid decreases. In spite of the fact that, after one month, the two solutions were almost identical in appearance, it is clear from the graphs that the changes had only proceeded about half way. Shuttleworth (44) states that they are complete only after 15 months: for this reason the solutions have been stored, and it is hoped that periodic analyses will be carried out on them.

The data from the pH curves seems to be in general agreement with that obtained from the conductometric studies. The tables below summarise most of the results obtained. The results obtained from the potentiometric titrations are shown in parentheses.

BOILED SOLUTIONS

Age	Initial pH	Initial Cond'ce x 10^3	Strong acid content (equivs)	Final end-point (equivs)
Zero	(2·64)	1·630	0·740	2·850
			(0·750)	(2·75)
1 hour		1·632	0·735	2·850
4 hours		1·635	0·725	2·850
1 day	(2·64)	1·669	0·715	2·850
8 days	(2·70)	1·629	0·710	2·880
30 days	(2·75)	1·584	0·590	2·890

UNBOILED SOLUTIONS				
Age	Initial pH	Initial cond'ce x 10^3	Strong acid content (equivs)	Final end-point (equivs).
Zero	(3·43)	1·606	0·215	3·010 (2·93)
1 hour		1·601	0·225	3·010
4 hours		1·590	0·240	3·010
1 day	(3·43)	1·489	0·250	2·990
8 days	(3·35)	1·370	0·275	2·980
20 days	(3·28)	1·398	0·315	2·975

The values of strong acid content of the fresh boiled solution obtained by the two methods agree reasonably well. It is therefore likely that the minima obtained in the conductance titrations have little significance in this respect. The two methods, however, give a small discrepancy in the amounts of NaOH required for the final equivalence point, the conductometric method giving the value more in agreement with that calculated.

In conclusion, it is suggested that conductometric titrations, carried out on solutions of the pure violet and green salts with $BaCl_2$ at temperatures near 0°C, would be very informative. In addition, similar titrations carried out with NaOH as titrant would yield very interesting results as the changes which take place in solution, and also the hydrolysis which occurs, would probably be arrested somewhat at low temperatures. The hydrolysis, at any temperature could, of course, be obtained by the method of Lamb and Fonda (loc. cit.) in which conductance measurements are taken on the solutions immediately after their preparation. As stated before, this method necessitates a special cell design.

GENERAL SUMMARY.

1) A constant temperature room, employing the comparatively new method of temperature control by means of a thyratron relay, has been constructed.

2) A high precision conductance bridge has been built in a very convenient form. Improvements include the incorporation of a cathode ray oscilloscope as null detector, and the inclusion of a very stable oscillator of the phase shift type, which is capable of giving a very pure wave form. Tests carried out on a system of degenerative tuning showed that the system is not easily applicable to high gain amplifiers.

3) A new form of conductometric titration cell, employing the dipping type electrodes, has been designed with special precautions against possible Parker Effect.

4) A series of tests has been carried out on three types of cell to ascertain the effects of adsorption, polarisation and Parker Effect on the accuracy of an ordinary conductometric titration.

5) Conductometric titrations of NaOH into solutions of violet and green chromic sulphate have been carried out, and the effect of ageing these solutions closely studied.

6) In addition, conductometric titrations of $BaCl_2$ into the chromic solutions have been made, and the NaOH titrations have been studied potentiometrically as well.

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