

From his measurements Watanabe calculates the free energy of formation of NiO(s) as  $\Delta F^\circ_{298.1} = -50,333$  cal., while Bogatskii's results lead to a value  $\Delta F^\circ_{298.1} = -52,092$  cal. Pease and Cook<sup>7</sup> have studied the reduction equilibrium with hydrogen at two temperatures, 485 and 600°, and from these data calculate for the formation of the oxide,  $\Delta F^\circ_{298} = -56,497$  cal. It will be noticed that the value obtained in this paper represents about the mean of the three previous determinations.

Kapustinskii and Novosel'tsev<sup>8</sup> have measured the heat capacity of NiO at temperatures from 373 to 1373°K. Their results can best be represented by the equation

$$C_p = 13.69 + 0.83 \times 10^{-3}T - 2.915 \times 10^5 T^{-2}$$

(7) Pease and Cook, *THIS JOURNAL*, **48**, 1199 (1926).

(8) A. F. Kapustinskii and K. A. Novosel'tsev, *J. Phys. Chem.*, *U. S. S. R.*, **11**, 61 (1938).

Using Kelley's<sup>9</sup> equations for Ni( $\alpha$ ) up to 626°K. and for Ni( $\beta$ ) above this temperature, and his equation for O<sub>2</sub>, we obtain

$$\begin{aligned} \text{Ni}(\alpha) + \frac{1}{2}\text{O}_2(\text{g}) &= \text{NiO}(\text{s}): \Delta F^\circ = -60,387 - 5.29T \\ \ln T + 2.85 \times 10^{-3}T^2 + 0.988 \times 10^6 T^{-1} + 52.84T \\ \text{Ni}(\beta) + \frac{1}{2}\text{O}_2(\text{g}) &= \text{NiO}(\text{s}): \Delta F^\circ = -59,692 - 2.55T \\ \ln T + 0.102 \times 10^{-3}T^2 + 0.988 \times 10^6 T^{-1} + 35.80T \end{aligned}$$

### Summary

1. The heat capacity of nickel oxide, NiO, has been measured from 68–298°K.

2. The entropy of the oxide is found to be 8.36 e. u., with an estimated accuracy better than  $\pm 0.1$  e. u.

3. The free energy of formation of the oxide has been calculated,  $\Delta F^\circ_{298.1} = -53,034$  cal., and has been expressed as a function of the temperature.

(9) Kelley, "Bureau of Mines Bulletin 371," 1932.

PITTSBURGH, PENNSYLVANIA

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[CONTRIBUTION FROM THE HAYDEN MEMORIAL LABORATORIES OF NORTHEASTERN UNIVERSITY]

## The Precision Conductivity Bridge Assembly

BY W. F. LUDER

### I. Introduction

The papers of Jones and Josephs<sup>1</sup> and of Shedlovsky<sup>2</sup> marked the beginning of a new era in the investigation of various chemical phenomena by means of conductivity measurements. The precision which they obtained was, and still is, sufficient for most such investigations. However, the rapid development of communication engineering since the publication of their papers has now made it possible to effect several desirable improvements in the whole conductivity bridge assembly. Furthermore, by taking advantage of recent developments, the expense and difficulty of assembling a complete bridge can be greatly reduced.

At about the same time as the work of Jones and Josephs and Shedlovsky on the conductivity bridge, an increased interest in many other types of alternating current bridges was evident in the large number of papers which were published each year. According to Hague,<sup>3</sup> well over 250 papers on a. c. bridge methods must have appeared since 1928. There were 48 in 1932

alone. One of the most thorough of the recent papers is that of Astin.<sup>4</sup> Although his bridge is of the Schering type, Astin has used a Wagner ground, and certain conclusions reached by him are of value in conductivity bridge design. Following Ogawa,<sup>5</sup> Astin has brought a. c. bridge theory to a high degree of perfection. In surveying this large field, however, chemists will do well to keep in mind the fact that the requirements of such bridges as those of Astin and of Balsbaugh and Herzenberg<sup>6</sup> are considerably greater than similar requirements for a conductivity bridge. The conductivity bridge is one of the simpler alternating current bridges.

Communication engineering has more than kept pace with requirements of low frequency a. c. bridges. The application of inverse feedback to the problem of tuning an oscillator or an amplifier<sup>7</sup> probably will be of value in many cases. It is doubtful, however, whether much advantage is to be gained by using it with the ordinary conductivity bridge. This is especially true in

(4) A. V. Astin, *Bur. Standards J. Research*, **21**, 425 (1938).

(5) Kazukiyo Ogawa, *Researches Electrotech. Lab. Tokyo*, No. 254 (1929); No. 277 (1930).

(6) Balsbaugh and Herzenberg, *J. Franklin Inst.*, **218**, 49 (1934).

(7) H. H. Scott, *Proc. Inst. Radio Engrs.*, **26**, 226 (1938).

(1) Jones and Josephs, *THIS JOURNAL*, **50**, 1049 (1928).

(2) T. Shedlovsky, *ibid.*, **52**, 1793 (1930).

(3) B. Hague, "A. C. Bridge Methods," Pitman, N. Y. (1938).

view of the fact that a very simple and inexpensive, low output, low harmonic-content oscillator is now available.<sup>8</sup> Constant-frequency oscillators, degeneratively tuned amplifiers, cathode ray tube null indicating devices, vibration galvanometers and similar complicated and expensive instruments are increasingly necessary in communication engineering and for use with Schering and other types of bridges. It is questionable, however, whether chemists have anything to gain by using them with the conductivity bridge.

sistors chosen, it is possible to keep the cost of the whole assembly below \$200.

### II. The Oscillator

Headphones and a high gain amplifier make the most convenient detector in a bridge assembly where they can be used to good advantage. This is certainly true for the conductivity bridge. When bridge balance is indicated by zero amplitude of a 1000 cycle note, it is important to keep all other sounds at a minimum level. Undesired noise in the phones comes from four principal sources: (1) harmonics generated by the oscillator or introduced by transformers, (2) a. c. hum, (3) stray pickup, and (4) tube noise. The first two arise primarily in the oscillator and its power supply; the others will be discussed subsequently.

Oscillators are generally considered satisfactory for most purposes if their harmonic content is less than 2-3%. This value is too high for a precise bridge balance unless a filter is used in the detector. Such filters in the past have been rather unsatisfactory. (The question of whether or not a tuned amplifier should be used will be discussed in Part III.) The use of degenerative tuning<sup>7</sup> has made possible the construction of oscillators with remarkably low harmonic content.<sup>9</sup> Such oscillators have other good features, among which are low hum level and more easily controlled and constant frequency. They are, however, somewhat complicated and expensive, and offer no advantages, for conductivity bridge use, over the oscillator shown in Fig. 1.<sup>10</sup> By careful adjustment of the regeneration control of this oscillator, the harmonics can be reduced to 0.1%. This is not necessary, however. With ordinary care the percentage distortion will be approximately 0.3%. No harmonics can then be heard when the bridge is balanced using an untuned three-stage amplifier (two 6J7's and one 6C5).

An easy method of reducing a. c. hum is to make the power supply for the oscillator of the constant voltage type. The constant plate voltage probably contributes, also, to the observed stability of the regeneration control. The circuit of a simple constant voltage power unit is given

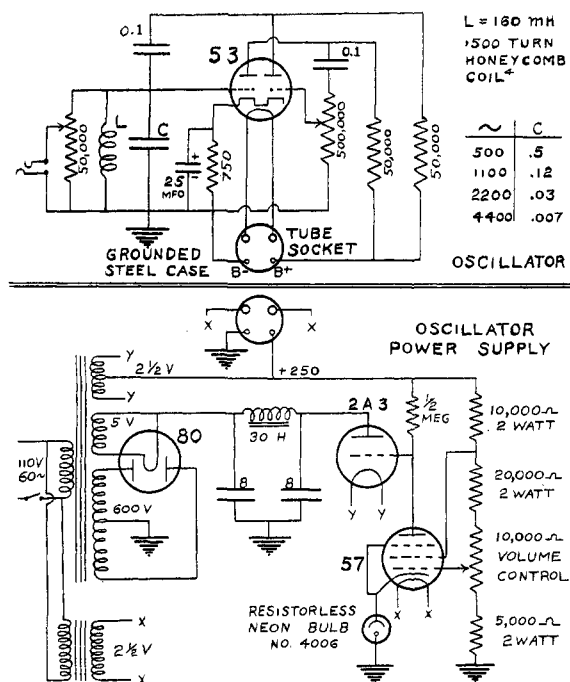


Fig. 1.

Securing the answer to this question was one of the objectives of the present investigation. Several different forms of the oscillator and its power supply, of the bridge network, and of the amplifier have been constructed and tested in this Laboratory. A preferred combination and several alternatives are suggested and discussed. Throughout the investigation the problem of easily duplicating the assembly as a unit has been kept in mind. Standard, readily-obtainable parts have been used. With the description given, any radio amateur or repair man should be able to complete the assembly in two or three days. This standardization has been secured with no loss in precision and with some gain in convenience in the operation of the bridge. Depending on the re-

(8) "Technical Service Bulletin TS-2," R. C. A. Manufacturing Co., Inc., p. 97.

(9) For example, in one commercial model, the General Radio 608-A, the harmonic content may be kept under 0.1%.

(10) The use of this oscillator was suggested by Professor Carl F. Muckenhoupt, Chairman of the Physics Department of Northeastern University. Acknowledgment is due the R. C. A. Manufacturing Co., Inc., Harrison, N. J., for their kind permission to reproduce the diagram from page 97 of their Technical Service Bulletin TS-2.

in Fig. 1. When the bridge is balanced using the oscillator and power supply shown in Fig. 1, each in a separate steel case connected by cable and plugs, no a. c. hum can be heard in the output of a three-stage untuned amplifier.

Therefore the first two sources of unwanted noise can be eliminated easily without the use of a complicated oscillator or a tuned amplifier.

A further consideration in the design of an oscillator for conductivity bridge use is its output voltage. Most oscillators will supply too much power to a conductivity bridge. The output voltage of the oscillator described, 0.5 volt or less, is about the correct value.<sup>11</sup> If the noise level can be kept low enough, an oscillator voltage of 0.5 volt is sufficient to give a sensitivity in bridge reading of one or two parts per million using a two-stage amplifier consisting of one 6J7 and one 6C5.

The operating characteristics of the oscillator are given. (No alternative is suggested for the oscillator and its power supply, because there seems to be no more suitable combination for use with conductivity bridges at the present time. In addition to its having the correct operating characteristics, this oscillator is simple, inexpensive, and easy to construct and operate.)

**Wave Form.**—With the regeneration control properly adjusted<sup>12</sup> and the fundamental frequency set at approximately 1100 cycles per second, the harmonic content in the output voltage is less than 0.3%.<sup>13</sup>

**Frequencies.**—Approximately 500, 1100, 2200, 4400 c. p. s., are obtained by selecting different capacitances by means of a dial switch on the front panel.<sup>14</sup>

**Output Voltage.**—With the regeneration control properly adjusted and the oscillator connected to the bridge through a General Radio type 578-B bridge transformer, the maximum output voltage at the transformer secondary is approximately 0.5 volt.

**Power Supply.**—Controllable constant plate supply type. At 250 volts d. c. output the a. c.

(11) Jones and Bollinger, *THIS JOURNAL*, 51, 2407 (1929).

(12) The adjustment is made by retarding the regeneration control until oscillation stops, then carefully advancing it until oscillation just begins again.

(13) A General Radio 736-A Wave Analyzer was used to make the distortion measurements. The author is indebted to Dr. Muckenhaupt for the use of the wave analyzer, a cathode ray oscilloscope, and a vacuum tube voltmeter.

(14) The inductance is a 1500 turn honeycomb coil ( $L = 160 \text{ mH}$ ) obtainable from the Radio Shack, 167 Washington St., Boston, Mass. Only rough observations were made on frequency stability, since conductivity measurements are not affected by small frequency changes.

line voltage may be varied between 85 and 130 volts without causing a variation of more than one volt in the oscillator plate voltage.

### III. The Amplifier

Since bridge balance is indicated by zero amplitude of the oscillator frequency, the useful gain of an amplifier is limited to a value not much greater than that at which the tube noise from the first tube becomes distinctly audible. This is true, of course, only if harmonics, hum, and stray pickup have been eliminated. Stray pickup will be discussed in Part IV.

The first amplifier constructed during this investigation was untuned and consisted of one 6J7 and one 6C5, supplied by batteries. Batteries were used because of the difficulties involved in preventing coupling between the oscillator and amplifier when both secure their power supply from a common a. c. source. "B" batteries are needed for a d. c. bridge with which to measure solvent conductance, at any rate. The same batteries may be used for the amplifier plate supply. The tube noise was just perceptible in this amplifier, which indicated that it had about the maximum useful gain that could be used without tuning. This gain was high enough to permit bridge balance to one or two parts per million in a quiet room. Therefore it is evident that when harmonics, hum, and stray pickup have been practically eliminated, such a two-stage untuned amplifier is sufficient for ordinary use of the bridge.

Little is to be gained by increasing the gain of the amplifier unless some means of tuning is employed. A three-stage untuned amplifier, constructed by adding another 6J7 tube to the two-stage amplifier, resulted in greatly increased volume of both the oscillator frequency and the tube noise. This may be of value if the bridge is to be used in noisy surroundings. However, in order to secure any great increase in sharpness of the bridge balance, a three-stage amplifier must be tuned. The best method seems to be degenerative tuning.<sup>7</sup> Inverse feedback is used to cancel all frequencies except that for which the degeneration network is balanced. Scott places the network around three direct coupled tubes in order to secure high selectivity. Direct coupling of three tubes, however, requires a very high voltage plate supply.

After some experimenting with degenerative

tuning, it seemed that the results in this case were not enough better than those obtainable by another method to justify the additional expense and difficulty of construction involved. This is particularly true with this assembly, since there is no need of suppressing harmonics from the oscillator. When noise other than tube noise has been practically eliminated from the assembly, the important requirement is a substantial reduction of tube noise with little decrease in signal strength. A simple method of tuning<sup>15</sup> which, although not extremely sharp, meets this requirement, is shown in the grid circuit of the 6C5 in Fig. 2.<sup>16</sup> Such an arrangement eliminates much of the background noise in the amplifier.

A number of such tuned circuits could be used for various frequencies by connecting them to a dial switch, but such an arrangement seems unnecessarily complicated. Most conductivity measurements are made at one frequency, usually 1000 cycles, so it seems best to include only one tuned circuit. A toggle switch is provided for

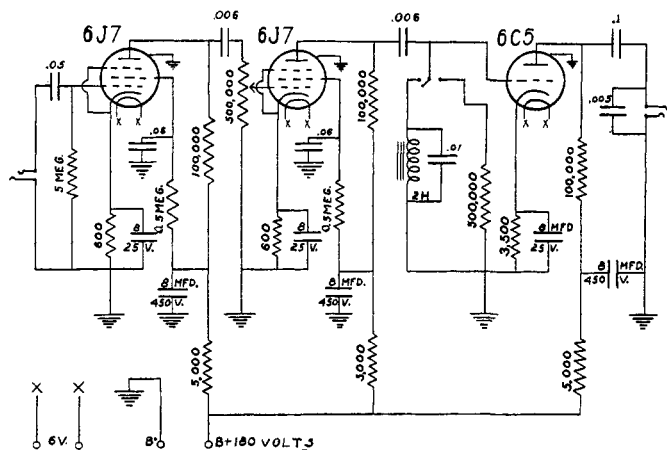


Fig. 2.

connecting a 500,000 ohm resistor in place of the tuned circuit. This permits the use of the amplifier as an untuned amplifier whenever measurements must be made at other frequencies.

An inductance of two henries is about right. This value can be obtained by increasing the separation between the I and E core pieces of a 10 henry, 50 milliampere, midget filter choke. If the frame is unclamped and seven strips of

(15) This method is a common one in communication engineering. It will not attenuate adjacent harmonics sufficiently if they are present to any great extent in the oscillator output.

(16) For a two-stage amplifier, one of the 6J7's and the tuned circuit should be left out. The choke, condenser, and switch should be removed and the grid connected directly to the 500,000 ohm resistor.

paper (cut to fit from typing paper) are inserted between the core pieces, the inductance will be about two henries. To tune this choke to 1,000 cycles a condenser of approximately 0.01 mfd. is needed. Since the inductance of the choke will not be exactly two henries, the correct value of the condenser should be chosen by experiment, starting with a value of 0.005 mfd. and adding 0.002 and 0.001 mfd. condensers in parallel until the correct value is reached. This is easily done by connecting the condensers while listening to the 1000 cycle note when the bridge is slightly off balance.

It seems that a two-stage amplifier is in many cases suitable. Where higher gain is necessary, sufficient tuning must be employed to reduce tube noise. Probably the most convenient method of tuning is the one described above.

#### IV. The Bridge Network

For most purposes there is no need of attempting to improve the precision obtained by Jones and Josephs.<sup>1</sup> There are, however, several refinements which may now be made. One of them involves a different method of connecting and balancing the Wagner ground circuit, called by Astin<sup>4</sup> separate balancing of the detector terminals to ground (Fig. 3). This method makes possible the elimination of the transformer usually employed between the bridge and the detector. A transformer in such a position is unsatisfactory for several reasons. Probably it is partly responsible for the fact that bridges using it show a great decrease in sensitivity as the resistance being measured is increased. At any rate, the bridge in the form now used in this Laboratory shows very little variation in balance sensitivity over its normal range of 1000 to 200,000 ohms. (Another factor in this nearly constant sensitivity will be referred to later.) A high impedance transformer is undesirable because of the effect stray fields may have upon it, thus making for a higher noise level.

If the more common form of Wagner ground described by Jones and Josephs<sup>1</sup> is to be retained, the elimination of the detector input transformer means that the amplifier cannot be grounded directly. Grounding a direct-coupled input amplifier makes the Wagner ground useless. An ordinary ungrounded amplifier, however, introduces

an intolerable amount of stray noise. An ungrounded, doubly shielded amplifier<sup>17</sup> may be used, but involves unnecessary difficulties of construction. An alternative is to wire the amplifier so that the B minus line is isolated from the grounded chassis. A 0.5 mfd. condenser is connected from the midpoint of the bridge ratio arms to ground. The B minus side of the amplifier is connected to the midpoint. This arrangement functions satisfactorily<sup>18</sup> except that the volume is cut down considerably when the Wagner ground is being balanced. This is because the low impedance of the condenser is then directly across the amplifier input. Astin has shown that the only effect of the large admittance of the capacitance to ground is to make the bridge balance more dependent upon the Wagner ground adjustment. The requirement for non-critical adjustment is that the ground admittances from the detector terminals must be similar in ratio to the ratio between the admittances of the arms in either of the two pairs between the detector terminals. The large admittance to ground of the 0.5 mfd. condenser makes the Wagner ground adjustment nearly as critical as it is when the detector terminals are balanced separately to ground. Therefore it seems best to adopt the separate terminal balance since a conventional grounded amplifier can then be used.

Separate balancing of the detector terminals to ground requires that the Wagner ground balance be adjusted as carefully as the bridge proper. This is easily done by using verniers  $R_2$  and  $C_2$  as shown in the bridge network arranged for separate terminal balance (Fig. 3). The bridge is balanced roughly with  $S_1$  upward. Then with  $S_1$  downward the Wagner ground adjustment is made, first roughly with  $C_1$  and  $R_1$ , then exactly with  $C_2$  and  $R_2$ . Finally with  $S_1$  upward again, the bridge is balanced exactly.<sup>19</sup> It is rarely necessary to repeat the procedure. ( $S_2$ , once set, is left untouched unless the oscillator leads are reversed.)

Jones and Josephs<sup>1</sup> and Shedlovsky<sup>2</sup> used 1,000-ohm resistors in the ratio arms and in the Wagner ground circuit of their bridges. It has

(17) Dye and Jones, *J. Inst. Elec. Engrs. London*, **72**, 169 (1933).

(18) No difference as great as 0.001% in measuring a resistance in the place of the cell can be detected when the frequency is changed from 500 to 4400 cycles.

(19) Those unfamiliar with separate terminal balance will be well repaid by a study of Astin's paper (ref. 4). (One of the Referees for this paper states that separate terminal balance was first proposed by Behr and Williams, *Proc. Inst. Radio Engrs.*, **20**, Fig. 13a, 985 (1932).)

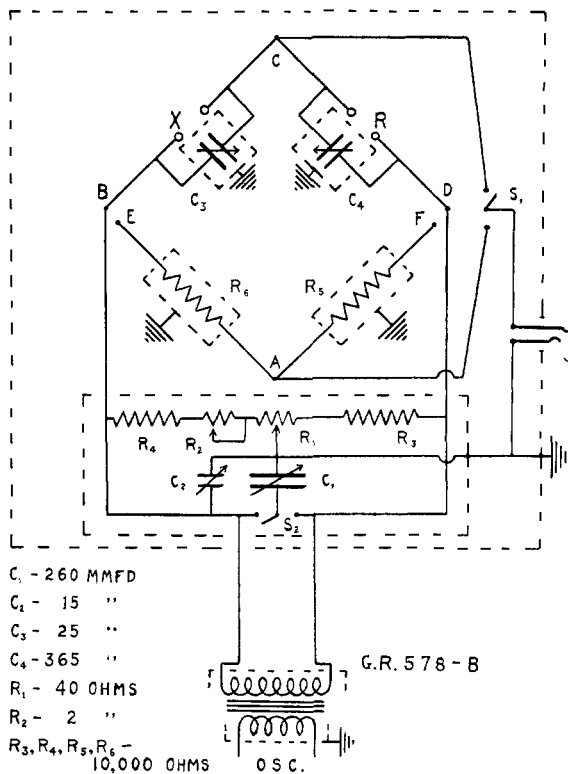


Fig. 3.

long been known<sup>20</sup> that one of the conditions for maximum balance sensitivity is to have the impedances of the four arms as nearly equal as possible. Therefore it seems desirable, for a bridge designed to cover the range of 1,000 to 200,000 ohms, to make the ratio arms and large Wagner ground resistances each equal to 10,000 ohms instead of 1000 ohms. When this combination is used with the readily available General Radio type 578-B bridge transformer step-up from oscillator to bridge, the oscillator-bridge impedance relationships are such as to give maximum energy transfer within the resistance range of the bridge.<sup>21</sup> This assists indirectly in making the bridge sensitivity comparatively constant. If the turns ratio of the transformer is such as to give maximum energy transfer from the oscillator to some impedance outside, or near one end of, the range represented by the bridge at the transformer secondary, considerable variation in apparent bridge sensitivity may be observed.

The chief source of stray pickup seems to be in the leads from the amplifier to the bridge and in the parts of the bridge connected directly to

(20) Reference 3, page 83.

(21) Different turns ratios of the transformer were tried, using a tapped telephone transformer.

these leads. For this reason, the shields around the ratio arms should be grounded directly instead of connected to the midpoint. Switch  $S_1$  should be a toggle switch, the frame of which is connected to ground. The connections to the amplifier should be made by shielded plugs and cable.

From the above considerations it seems preferable: (1) that the Wagner ground be of the separate terminal balance type, (2) that 10,000 ohm resistances be used in the ratio arms and Wagner ground circuit, (3) that thorough shielding be employed. A description of the bridge control panel constructed by the author utilizing these features follows.

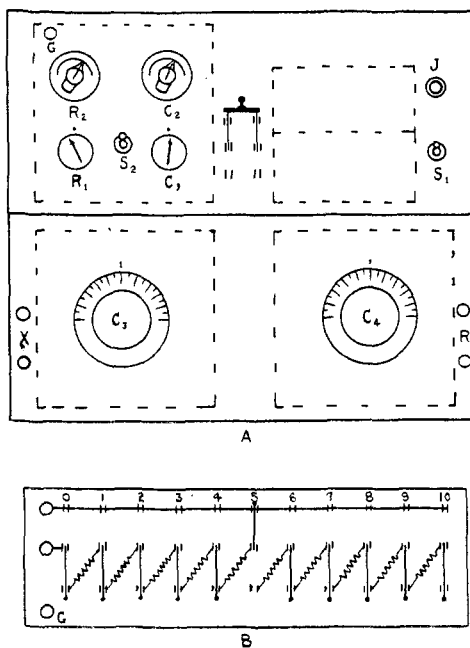


Fig. 4.

The panel itself consists of two  $7'' \times 18'' \times \frac{3}{16}''$  ( $18 \times 45 \times 0.5$  cm.) hard rubber radio panels bolted together by means of a hardwood frame under the two panels (Fig. 4). The Wagner ground assembly is contained in one standard  $6'' \times 6'' \times 6''$  ( $15 \times 15 \times 15$  cm.) radio shield bolted to the panel underneath the farther left-hand corner.  $S_2$  is a toggle switch.  $R_1$  and  $R_2$  are ordinary radio potentiometers. Each balancing condenser is contained by itself in a  $6'' \times 6'' \times 6''$  shield. The farther right-hand section of the panel is shielded by copper sheet under the panel. It carries the ratio-arm shield, the jack for the amplifier plug and the toggle switch  $S_1$ . The ratio-arm shield is constructed of sheet copper just enough smaller than the other three shields to leave room for the switch and jack. The shield is divided into two compartments by a sheet of copper. Each compartment contains one of ratio arms. The reversing switch for the ratio arms<sup>2</sup> is a double-pole-double-throw knife switch mounted above the panel near the center. It is so connected as to reverse

the connections E and F (Fig. 3) to B and D. The 10,000 ohm resistors are General Radio type 500-J without their cases. The two employed as ratio-arms should be so chosen (from the group to be used in constructing resistance boxes) as to have as nearly identical resistances as possible.

The walnut case which contains the control panel assembly is lined with thin sheet copper connected to the common ground. Shielded cable is used for the oscillator leads. The bridge transformer is connected step-up to the bridge from the oscillator. Its primary shield is grounded, its secondary shield is left floating. The transformer is placed about midway between oscillator and bridge. With this assembly it has not been found necessary to keep the bridge more than ten feet (3 meters) from the oscillator. The oscillator power supply is about five feet (1.5 meters) from the oscillator.

Suitable resistors are now produced by two companies: Leeds and Northrup and General Radio. General Radio resistors were used in this investigation. According to the General Radio catalog, their resistors have a higher temperature coefficient than Leeds and Northrup resistors, but are less expensive.<sup>22</sup> The temperature coefficient is not so high that thermostating is necessary, unless extreme precision is desired. Humidity changes sometimes cause greater changes in resistance than do temperature changes. In observations of the resistance of a sealed 10,000 ohm resistor measured against a combination of unsealed decade resistors no definite humidity effect could be noted. An extra precaution would be to dip the higher resistors in paraffin.<sup>23</sup>

A standard 602-F decade box is suitable for the three lowest decades (0.1, 1, 10 ohm steps). For the 100 ohm and 1000 ohm step decades, 510-D and 510-E decades were modified as follows. Each decade was removed from its close-fitting shield and mounted in a  $6'' \times 6'' \times 6''$  radio shield. In the 1000 ohm step decade, in order to move them farther apart, alternate resistors were unsoldered and replaced projecting outward. The shields were then bolted together to make one two-dial decade box. Two 100,000 ohm resistance boxes were constructed using ten 10,000 ohm resistors in each.<sup>24</sup> The resistors were connected to small knife switches as suggested by Jones and Josephs<sup>1</sup> and shown in Fig. 4-B. Throwing only one switch gives the desired resistance without leaving any dead-end resistances. The wooden boxes are lined with grounded copper sheeting, but fortunately it is unnecessary to attempt to shield panel and switches. Unshielded leads are used between the resistance boxes.

(22) The temperature coefficient for Leeds and Northrup resistors is given as 0.0001% (Dike, *Rev. Sci. Instruments*, **2**, 393 (1931)). For General Radio resistors, the value is given as "less than 0.002%." Dike states that the Leeds and Northrup resistances are wound with manganin wire. In the specifications for their decade units, the General Radio catalog states that the lower resistors are wound with manganin wire and the 10,000 ohm cards with a combination of Nichrome and Ohmax to give "nearly zero" temperature coefficient. Therefore, in view of the fact that the General Radio Company is usually conservative in its performance claims, it seems probable that the temperature coefficients are considerably less than the value 0.002% given.

(23) Reference 3, p. 103.

(24) General Radio type 500-J resistances may be obtained without cases. Their a. c.-d. c. resistance difference is less than 0.1% at 50 kilocycles. Therefore, at one kilocycle it should be less than 0.001%.

Shielding of the network from stray pickup together with the absence of harmonics and hum from the oscillator have made it possible to balance the bridge to one or two parts per million using only the two-stage untuned amplifier described. When the bridge is at balance using this amplifier, no sound other than the barely perceptible hiss of the tube noise can be heard in the phones, even though the amplifier is untuned.

### V. Summary

1. The conductivity bridge assembly has been investigated to determine to what extent it is advantageous for chemists to employ recent complicated and expensive developments in communication engineering in such a simple type of alternating current bridge.

2. Several different forms of the oscillator and its power supply, of the bridge network, and of the amplifier, incorporating recent developments in a. c. bridge methods and communication engineering, have been constructed and tested.

3. An adaptation of a new and simple low-distortion oscillator to conductivity bridge use is

described. The oscillator plate supply is of the constant voltage type to reduce a. c. hum and stabilize the regeneration control.

4. Separate detector terminal balance to ground is suggested for conductivity bridges, and its adaptation and use described. The use of 10,000 ohm instead of 1,000 ohm resistors for the ratio-arms and Wagner ground circuit is proposed. Shielding to reduce stray pickup to a minimum is described.

5. A two-stage untuned amplifier with gain sufficient to permit balancing the bridge to one or two parts per million when oscillator harmonics, a. c. hum, and stray pickup have been practically eliminated is suggested for ordinary use of the bridge. A description of a three-stage tuned amplifier is also given.

6. Simplification, ease of construction, and lowered cost have been attained with no loss in precision and with some gain in convenience in the operation of the bridge.

BOSTON, MASS.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF NEW HAMPSHIRE]

## The Magnetic Rotation of Praseodymium, Samarium, and Europium Chlorides in Aqueous Solution at 25°

BY CHARLES M. MASON, JOSEPH W. HICKEY AND WILFRED K. WILSON

Recently<sup>1</sup> this Laboratory has presented the results of an investigation of the magnetic rotation of lanthanum and neodymium chlorides in aqueous solution. In the present work this method of investigation has been extended to the aqueous solutions of praseodymium, samarium, and europium chlorides. The Verdet constants have been obtained for these solutions over a concentration range from zero (pure water) to 3.5 molal. The dispersion has been studied from 4811 to 6438 Å.

### Experimental Details

The rotations were measured with a Franz Schmidt and Haensch model 55 Landolt-Lippich triple-shadow polarimeter with non-magnetic frame. The instrument could be read to one-hundredth degree of arc. The light sources used were a mercury Lab-Arc, sodium Lab-Arc, and a Zeiss electrical spectral lamp fitted with Osram zinc and cadmium-filled bulbs. Monochromatic light was obtained by means of a Winkel-Zeiss monochromator inserted in the optical path between the spectral source and the polar-

imeter. By this means it was possible to isolate the principal lines of the various spectra with enough intensity left to properly operate the polarimeter.

The solution, the rotation of which was to be measured, was placed in a water-jacketed cell of Pyrex brand glass equipped with optical windows of the same material fused to the ends of the cell. This cell, as placed in the magnet, is shown in Fig. 1. The magnet consisted of 17 layers of approximately 162 turns each of No. 16 B. and S. gage, silk-covered copper wire wound on a bakelite tube 3.5 cm. inside diameter and 24 cm. long. The total number of turns was 2753 and the length of the coil was 23.1 cm. The length of the light path through the solution was 20.08 cm. measured by calibrating the tube with carefully purified sucrose. These data enabled the computation of the field strength,  $H$ , of the coil at any point along the axis. The product of the effective field strength times the length of the light path in the cell was determined by integration between limits based on the diameter of the first and last layers of turns to be 11,089.4 gauss. Integration for each layer of turns and summation gave a value of 11,084.6 gauss, a check well within the experimental error of the methods used to measure the angle of rotation. This field strength, when used to compute the Verdet constant of water, gave a value of  $13.11 \times 10^{-3}$  for that constant at 25° and wave length 5893 Å. This com-

(1) C. M. Mason, R. D. Gray and G. L. Ernst, *THIS JOURNAL*, **58**, 1600 (1936).