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[Contribution from the Chemical Laboratory of Washington Square College, New York University]

A VACUUM TUBE POTENTIOMETER FOR RAPID E.M.F. MEASUREMENTS[1]

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Applications of one or more triode valves to various forms of apparatus suitable for the determination of *P*H values, electrode potentials, electrotitrations and the like have been described by several writers.[2] Nearly all of these require a calibration of the valves, are dependent upon the constancy of the characteristics of the valves and require sources of filament and plate potentials which will not vary over a considerable period of time. These limitations have been the motive for the development of the apparatus herein described and which has the following attributes: (a) it is a direct reading, no current device; (b) it is independent of the characteristics of the valves and of their power supply; (c) the "balance" condition is definite and very stable; (d) since the e.m.f. is read directly from a voltmeter in the grid circuit of the first (four element) tube, the values obtained will be dependent on the precision of this meter; (e) the maximum current taken from the cell is of the order of 10^{-9} ampere—at "balance" it is 0. The unknown cell may, therefore, be left continually in circuit during the balancing, which requires only a single operation; (f) the resistance of the cell under measurement is unimportant. No difficulty has been experienced in measuring the e.m.f. of a cell containing two glass electrodes; (g) when used with a cell containing properly prepared electrodes, *P*H values may be rapidly determined and are reproducible to 0.02 of the Sörensen unit.

Principle of Operation

In place of the conventional "bridge" a vacuum tube amplifier consisting of a tetrode and a triode is substituted. For a more complete descrip-

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[1] Presented at the Fall Meeting of the American Chemical Society held at Swampscott, Massachusetts, September 13, 1928.

[2] Van der Bijl, "The Thermionic Vacuum Tube," McGraw-Hill Book Co., Inc., New York, **1920**; Goode, This Journal, **44,** 26 (1922); **47,** 2483 (1925); Fitch, *J. Opt. Soc. Am.*, **14,** 348 (1927).

tion of the operation of the valves than will be attempted here, the reader is referred to a text on wireless communication or to the articles by Goode. Several of the more common types of broadcast receiver tubes can be adapted to this work, but after a study of the characteristics of different audions, the types "−22" and "−20" were, respectively, selected. A of Fig. 1 shows the mutual conductance curve for the "−22" type of valve.

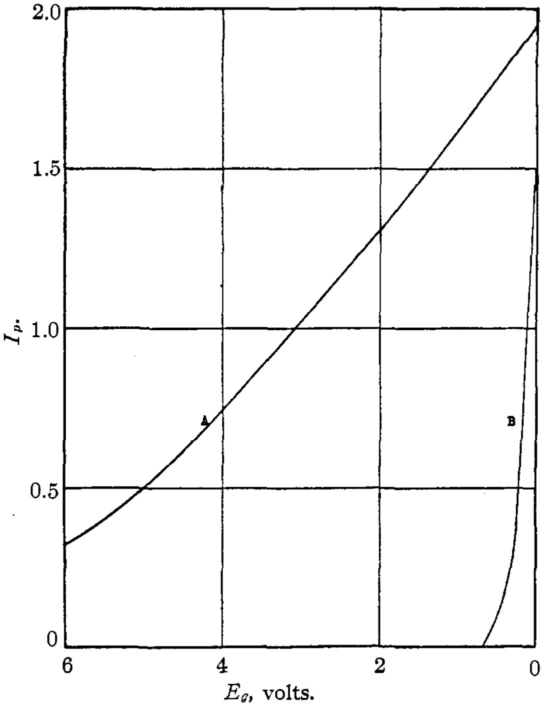

Fig. 1.

A—Grid voltage-plate current characteristic for shielded plate valve, plate voltage = 135 volts; outer grid voltage = 45 volts; inner grid voltage = E_g. B—Grid voltage-plate characteristic of vacuum tube potentiometer. E_g = potential applied between inner grid and filament of tetrode. I_p = plate current of triode in milliamperes.

The inner grid of the four element tube is used as the control grid. The outer grid is made positive with respect to the filament by 45 volts. The plate is operated at a potential of 135 volts. If the inner grid of this tube is connected directly to the negative lead of the filament, the resulting grid voltage is zero and a glance at the curve shows that the plate current under these conditions is 1.95 milliamperes. If now a cell with an unknown e.m.f. is connected between inner grid and filament with the negative side toward the grid, an unknown negative grid voltage results and the plate current drops to some lower value. An extremely feeble current will, under these conditions, be drawn from the cell being measured. A source of variable potential supplied by a dry cell or a storage cell and spanned by a voltmeter is inserted in the grid-filament circuit in such a manner that the variable potential opposes the unknown e.m.f. The variable potential is altered until the plate current again becomes 1.95 milliamperes. The unknown cell is now giving no current and the true e.m.f. of the cell may be read directly from the voltmeter. The measurement is also independent of the characteristics of the valve since the initial and final plate current values are identical, and are represented by a single point on the mutual conductance curve. The assumption is made, of course, that the tube characteristics and batteries have remained constant during the minute or so which has been spent in taking the readings. As a precautionary measure, a simple switch is provided by which the operator may, in a few seconds, check the plate current value before and after each reading. A more complete description of this procedure will be found elsewhere in the paper.

Actually, two valves are employed in such a manner that the variation in plate current of the tetrode is amplified by the triode. Curve B of Fig. 1 shows this change in plate current in the triode with accompanying variation of grid potential at the tetrode. The increased sensitivity of this arrangement over that of a single tube is apparent by contrasting the slopes of the two curves of Fig. 1. Obviously the actual principle of operation is the same as if a single tube were used.

Apparatus and Circuit Constants

The circuit employed is shown in Fig. 2. The filaments of both tubes are heated by battery A, which consists of three ordinary lead storage cells. A 20-ohm rheostat F regulates the potential applied to the filaments, which should be operated at 3.3 volts for maximum useful life and efficiency. The plates of the valves are supplied from batteries B_1, B_2 and B_3, which may be "B" batteries of the type used for broadcast reception and having values of 45, 22.5 and 67.5 volts, respectively. Storage cells may be used if preferable but they must be kept free from dust and charging spray or troublesome leakage will result. The plate current of the triode is registered on the milliammeter MA, which should have a full-scale deflection for 1.5 milliamperes. The absolute precision of this instrument is of secondary importance since no direct readings of the plate current need be taken. Coupling resistance R is a 100,000-ohm wire-wound resistance of the cartridge type having a small temperature coefficient and capable of dissipating 0.75 watt. The apparently large power rating of this resistance is specified to make certain that there is no rise in temperature due to the plate current of the tetrode, which it is continually required to pass.

If the grid and filament of the tetrode are connected together, the magnitude and direction of the current through resistance R is such that too great a negative potential is applied to the grid of the triode to allow any plate current to flow through MA. In order that MA may show full-scale deflection, the grid of the tetrode will have to be negative with respect to its filament by a value between two and three volts. This is accomplished by the 400-ohm "potentiometer" C with its winding spanning resistance F. The values selected for the source of the opposing potential O, for the voltage divider D and for the voltmeter V will depend upon the e.m.f. of the cell E which is to be measured. For values up to six volts, D also may be a good grade "potentiometer" of the broadcast receiver type. For all *P*H work and for most work in determining electrode potentials, the opposing battery O may be a single dry cell or a storage cell. The choice of the voltmeter V will depend upon the range of voltage to be covered and the accuracy desired. The writer has found the Weston Model I "Electrolysis Voltameter" with its five voltage ranges a very useful instrument, although some other types of meter are capable of a little better precision. The switch S is of the single pole double-throw type with its blade connected to the grid as shown in Fig. 2.

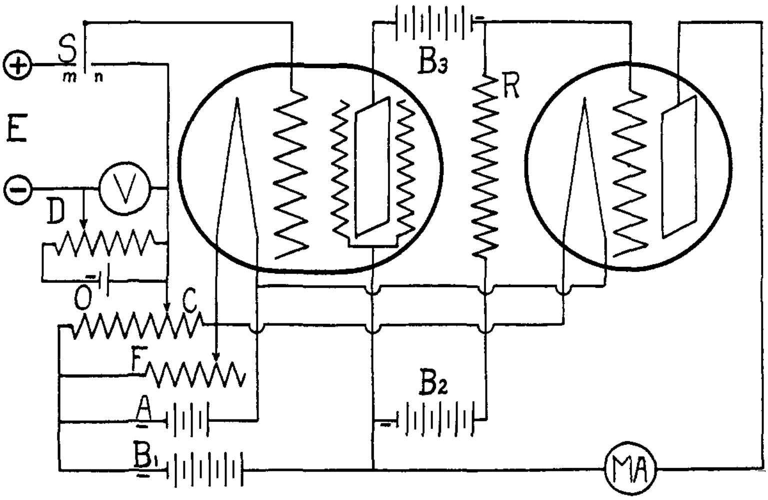

Fig. 2.—Diagram of connections.

Operation

If the circuit has been properly connected, the milliammeter MA should read zero when the switch S is thrown to position n and the slider arm of C is in such a position that it is directly connected with the filaments of both valves. If the slider arm of C is cautiously advanced toward the battery end of the winding, a point will be found at which MA will register nearly 1.5 milliamperes. If the cell E whose e.m.f. is to be measured has been attached in the proper manner and with the switch S connecting it to the circuit at m, the reading of MA is reduced in magnitude.. The switch S is now thrown to n so that it connects grid and filament directly through C and the reading on MA noted. For convenience C may be adjusted until the needle of the milliammeter is exactly coincident with a marked value on the scale, for example, 1.4. The switch S is returned to its former position, m, and voltage divider D is advanced until the triode plate current has reached its former value, 1.4. Care should be taken not to force the plate current meter off the scale lest it be damaged. The reading on the voltmeter V at this point registers the e.m.f. of cell E.

Advantages

The device described herewith is somewhat more convenient than most vacuum tube potentiometers for chemical measurements in that the valves do not have to be calibrated and it is not essential that their characteristics remain constant over long periods. It is considerably more rapid than the average potentiometer in that only one adjustment is necessary for one measurement. Owing to the conditions under which the device is operated, the maximum current taken from the cell is exceedingly small. It may be used for the measurement of a cell whose internal resistance is too great to allow it to be measured by a potentiometer employing the conventional Poggendorf system. Glass electrodes furnish such an example. W. S. Hughes[3] has found that the average glass electrode made from soft glass has a resistance of between 23 and 100 megohms. In this connection curves are given in Figs. 3 and 4 plotted from data obtained in neutralization titrations employing glass electrodes. Fig. 3 is an HCl–NaOH ti-

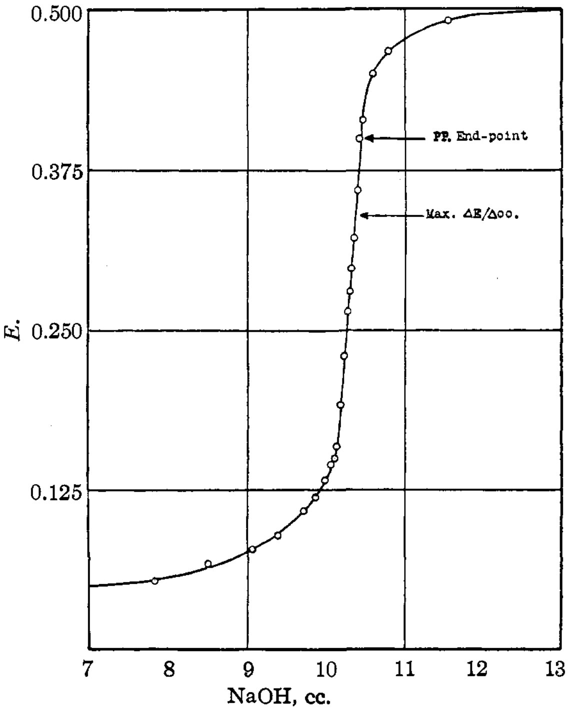

Fig. 3.—Neutralization of hydrochloric acid.

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[3] Hughes, This Journal, **44**, 2860 (1922).

tration employing one calomel and one glass electrode. Fig. 4 represents an NaOH–acetic acid neutralization in a cell containing two glass electrodes. While the points in the latter case do not represent a curve remarkable for its smoothness, they were obtained under conditions of extreme atmospheric humidity and electrical disturbances which would make the electrometer, ordinarily used for glass electrode measurements, quite useless.[4] For a more complete discussion of the glass electrode the reader is referred to papers by Watson and others.[3,5]

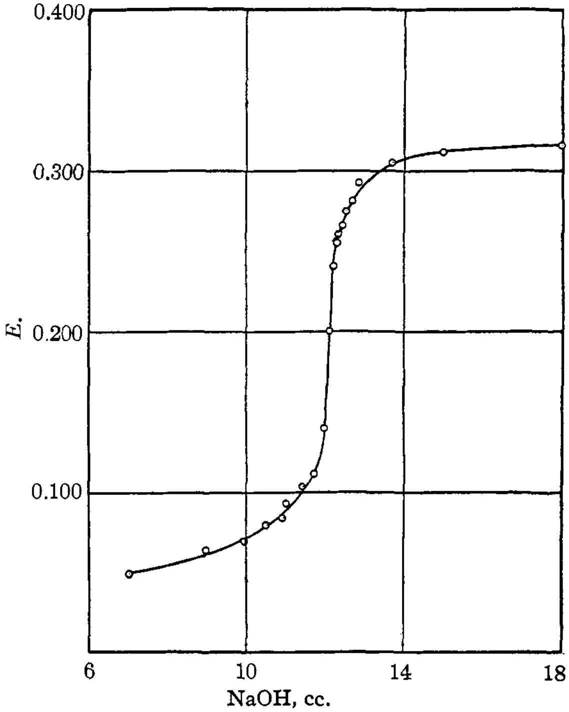

Fig. 4.—Neutralization of acetic acid—cell containing two glass electrodes.

Precautions

No trouble should be experienced from leakage if the apparatus is used on a dry wooden table. If, however, it is desirable to employ the potentio-

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[4] If greater accuracy is desired than can be obtained with a voltmeter, V, D and O of Fig. 2 may be substituted by a potentiometer connected in such a manner that a known potential opposes E. If MA has 150 scale divisions for 1.5 milliamperes, an accuracy of 0.00015 volt will be obtained.

[5] Watson, *Chem. Eng. Mining Rev.*, **20**, 59–62 (1927); Kerridge, *Biochem. J.*, **19**, 611 (1925); *J. Sci. Instruments*, **3**, 404 (1926); Bayliss, Kerridge and Conway-Verney, *J. Physiol.*, **61**, 448 (1926); Brown, *J. Sci. Instruments*, **2**, 12 (1924); v. Steiger, *Z. Elektrochem.*, **30**, 259 (1924); Horowitz, *Z. Physik*, **15**, 369 (1923).

meter on a stone-topped table or upon one which has at some time been bespattered with reagents, careful insulation of all batteries from each other and from the table will be necessary. All wiring should be done so that conductors do not touch one another even though they carry "insulation." The cell E to be measured should be placed upon a dry hardwood board, hard rubber or other insulating material. Due to the high amplification obtained, the valves should be kept as free as possible from mechanical vibration. The inner grid of the tetrode should be connected with flexible wire. In some instances connecting the negative side of the filaments to earth may be helpful although in all work done by the writer this has been found unnecessary.

Summary

A device has been described which employs a tetrode and a triode in a simple potentiometer circuit and arranged in such a manner that calibration of the valves and the constancy of their characteristics are unnecessary. Since the apparatus is essentially electrostatic in operation, it is particularly adapted to the measurement of cells having high internal resistance. As only one adjustment is necessary, measurements may be made with comparative rapidity.

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THE SYNTHESIS OF WATER WITH A SILVER CATALYST. II. ENERGY OF ACTIVATION AND MECHANISM

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Introduction

In a number of examples of homogeneous, bimolecular gas reactions it has been shown[1] that the absolute rate of reaction may be expressed by the equation

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = Ze^{-\frac{E}{RT}}$$

where C is the concentration of the reacting species at time t, Z is the number of collisions in unit time per unit of volume, and E is the energy of activation per two moles of reactant. $e^{-E/RT}$ is, therefore, the fraction of the total number of collisions which is effective. Since the fraction of the molecules which have energy of any particular kind, kinetic, rotational, vibrational or electronic, in excess of E calories per mole is also approxi-

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[1] Lewis, *J. Chem. Soc.*, **113**, 471 (1918); Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, **1926**, pp. 50 *et seq.*