LABORATORY AND PLANT

AUTOMATIC METHODS OF GAS ANALYSIS DEPENDING UPON THERMAL CONDUCTIVITY[1]

By E. R. Weaver, P. E. Palmer, H. W. Frantz, P. G. Ledig and S. F. Pickering

BUREAU OF STANDARDS, WASHINGTON, D. C.

Received August 19, 1919

PRINCIPLE OF THE METHOD

When a wire, surrounded by a gas enclosed in a space the walls of which are at constant temperature, is continuously traversed by a constant electrical current, the wire rises in temperature until a state of equilibrium is reached, in which the continuous dissipation of thermal energy is equal to the electrical energy supplied. This dissipation of energy takes place in the four following ways:

1—By radiation.

2—By conduction through the connections to the ends of the wire.

3—By thermal convection, i. e., by currents of gas circulating in the atmosphere surrounding the wire.

4—By conduction through the gas.

In case there is a flow of gas past the wire, heat is also carried away by the gas stream.

By a proper choice of conditions, all loss of heat except by conduction through the gas surrounding the wire may be reduced to a small portion of the whole. The equilibrium temperature attained by the wire will then depend mainly upon the thermal conductivity of the gas which surrounds the wire, being lower when the gas has a high conductivity and higher when the gas has a low conductivity. Since the coefficients of thermal conductivity of various gases and gas mixtures differ widely (Table I), the temperature of the wire will be determined by the composition of the surrounding gas. If, now, the wire has a high temperature coefficient of electrical resistance, its resistance to the passage of a constant current of electricity, depending as it does on the temperature of the wire, will have a value corresponding to the thermal conductivity, and therefore to the composition of the surrounding gas or gas mixture.

TABLE I—THERMAL CONDUCTIVITY OF GASES
(From Smithsonian Physical Tables)

GAS	$k_t \times 10^4$
Air	0.568
Argon	0.389
Ammonia	0.458
Carbon monoxide	0.499
Carbon dioxide	0.307
Ethylene	0.395
Helium	3.39
Hydrogen	3.27
Methane	0.647
Nitrogen	0.524
Nitrous oxide	0.350
Oxygen	0.563

(k_t is the heat in gram-calories flowing in 1 sec. through a distance of 1 cm. per sq. cm. for 1° C. drop in temperature.)

Inasmuch as electrical circuits are easily arranged for the rapid and very accurate determination or comparison of the resistance of such a wire, the quantitative determination of the constituents in a wide variety of gas mixtures whose qualitative composition are known is possible by a simple and exceedingly sensitive method based upon the thermal conductivity of the mixtures.

HISTORY OF THE METHOD

Schleiermacher[1] developed a method for determining the thermal conductivities of gases by utilizing the fact that a platinum or nickel wire stretched along the axis of a glass tube immersed in a water bath assumes a temperature, when heated by an electric current of constant strength, which depends upon the nature of the gas surrounding the wire. Goldschmidt[2] improved Schleiermacher's original method by comparing two wires of different lengths inclosed in silver capillaries inserted in a massive brass block. This improved method was used by Eucken[3] in his experiments on the thermal conductivity of gases. The use of thermal conductivity for gas analysis was probably first suggested by Leon Sowzee about 1880. Unfortunately a description of his method is not available since the report of the Prussian Fire Damp Commission, in which the only known reference to it occurs, gives no details. The Vereinigte Maschinenfabrik, Augsburg, patented in Germany[4] and England[5] the use of the thermal conductivity of a gas containing hydrogen to obtain an indication or a record of the variation in composition of a gas mixture. Several devices are specified, in one of which the resistance of an electrically heated wire in a closed tube is measured. This firm appears, however, to have been unsuccessful in applying the method. A. Koepsel[6] developed an apparatus for the determination and continuous indication of the hydrogen content of producer gas, which he stated was capable of easily detecting the presence of 0.001 per cent of hydrogen without the use of very refined measuring apparatus. He also proposed the application of his apparatus to the determination of carbon dioxide in flue gases and of methane in mine gases, but did not demonstrate experimentally the feasibility of his proposals. In its most improved form, Koepsel's apparatus consisted of four electrically heated wires exposed in pairs to the two gases to be compared, the two wires of each pair being connected to form opposite arms of a Wheatstone bridge. Koepsel's apparatus was particularly designed for use in a rather rapid gas stream and rather elaborate housings were arranged for the wires to shield them from the effects of convection. Siemens and Halske[7] improved Koepsel's apparatus by passing the gases going to the two sides of the bridge through tubes in the same metal block to bring them to the same temperature, and eliminated Koepsel's special housing for the wires.

[1] Wied. Ann., 34 (1888), 623; 36 (1889), 346.

[2] Physik. Z., 12 (1911), 417.

[3] Ibid., 12 (1911), 1101.

[4] D. R. P. 165,349 (1904).

[5] Brit. Patent 15,706 (1904).

[6] Ber. physik. Ges., 10 (1908), 814; 11 (1909), 237; Z. Chem. apparat., 3 (1908), 377, 401; Chem. Abs., 2 (1908), 3212; 3 (1909), 1108, 2646.

[7] D. R. P. 283,677 (1913).

In 1915 or 1916 the Sperry Gyroscope Company developed an apparatus similar to that of Siemens and Halske for detecting hydrogen in air. About the same time, but before learning of the work of this company, some investigations along the same line were begun at the Bureau of Standards but were abandoned because the delicacy of the indicating instrument required made it unsuitable for the immediate purpose in view. In ·the first months of 1917 a gas analysis apparatus utilizing the thermal conductivity principle was developed by a group of men at the University of California, was submitted to the Navy Department, and was tried out successfully for a number of purposes. In this instrument, which was extremely simple, two arms of the Wheatstone bridge consisted of wires stretched in the axes of metal tubes and exposed to the gases to be compared; the other two arms of the bridge were fixed external resistances. Prof. G. A. Shakespear[1] of Cambridge, England, has developed an apparatus similar in principle to that of the "University of California Hydrogen Detector," though of more compact construction, small platinum coils being substituted for the straight wires used in the earlier instrument.

As far as it is known, these investigators confined their methods to the use of a Wheatstone bridge with fixed resistances, depending upon the deflection of a galvanometer or millivoltmeter for indicating the relative resistance of the heated wires exposed to the gas to be analyzed and to a "standard gas," usually air.

About the first of January 1918, work was begun at the Bureau of Standards to utilize a thermal conductivity method in connection with a number of problems, and in addition to the schemes used by the other investigators, a number of other combinations were tried; and what is believed to be the most generally useful form of apparatus was arrived at by a process of elimination.

The history of this development is given in such detail in order to clear up a situation which might otherwise give rise to ill feeling. It is known that one of the recent experimenters believed himself the first to utilize heat conductivity measurements for making gas analyses until his apparatus was submitted to the Bureau of Standards for test, and a similar claim has been repeatedly made for another investigator, though not by the investigator himself.

In July 1918, at the request of the Nitrate Division of the Ordnance Department of the Army, the solution of the problem of the continuous analysis of the gases was undertaken for the analytical control of the synthetic ammonia plant being erected at Sheffield, Alabama. It was planned to use the thermal conductivity method for much of this work. At the time of the signing of the armistice when work on the ammonia plant was discontinued, the apparatus had been constructed and calibrated and was practically ready for installation in the plant.

The feasibility of using the method for the continuous analysis of the gases at different stages in the

separation of helium from natural gas was indicated by a few experiments. At the request of the Navy Department, this application of the method was developed, and apparatus for determining and automatically recording the percentage of helium in helium-nitrogen mixtures was built, calibrated, and installed in one of the helium extraction plants where it is reported to have given very satisfactory service for several months. Work has started on the construction of equipment for a 16-point analytical control apparatus for installation in another helium plant.

As opportunity has offered, experiments have been made to ascertain the applicability of the method to various important industrial processes. The uniform success which has been obtained indicates that its field of usefulness extends to a large number of operations and processes where a knowledge of changes in composition of gas mixtures is desired.

DESCRIPTION OF ELECTRICAL ARRANGEMENTS

WHEATSTONE BRIDGE WITH INDICATOR—In the device suggested by Koepsel[1] the indications of the changes in composition of a gas mixture were obtained in the following manner: Four wires of like material, cross-section, and length constituted the arms of a Wheatstone bridge. Two of the wires, forming opposite arms of the bridge, were placed together in a cell through which passed a current of the gas for analysis; the other two wires were placed together in a cell through which passed a comparison gas. Thus the differences in thermal conductivity of the gases in the two cells resulted in a maximum of unbalance of the bridge. An instrument calibrated to indicate directly the percentages of a constituent of the gas mixture of variable composition replaced the customary galvanometer. Since the resistance of the wire is very materially affected by changes in the current strength, the current must be carefully adjusted and maintained at a definite value. Koepsel used a battery as a source of constant current and avoided the use of an additional current-measuring instrument by providing a resistance coil between the battery and the bridge across the terminals of which the indicator could be switched. Current through the bridge was adjusted by means of a rheostat in the battery circuit until the deflection of the pointer of the indicator reached a certain mark on the scale. Fig. 1 shows diagrammatically the arrangement of the apparatus.

This arrangement, which is essentially the same as that developed by the other investigators mentioned, has many limitations. In order that the apparatus may detect small changes in the composition of the gas mixture, the indicator must have a high sensitivity, making it a necessarily expensive instrument, and since there must be a special scale for each gas and each range of gas percentages if the apparatus is to indicate percentages of the desired constituent directly, it becomes impracticable to use the same instrument for the determination of more than a very few constituents in a gas mixture and only over a

[1] U. S. Patent 1,304,208 (1919).

[1] *Loc. cit*

small number of ranges. Furthermore, the usefulness of apparatus for the analysis of gas mixtures whose composition is continuously changing is frequently dependent upon whether the apparatus can be arranged to provide a record of the changes in gas composition, to actuate control mechanisms, or to positively sound an alarm. For these purposes neither Koepsel's apparatus nor any other apparatus utilizing the same type of bridge arrangement is suited.
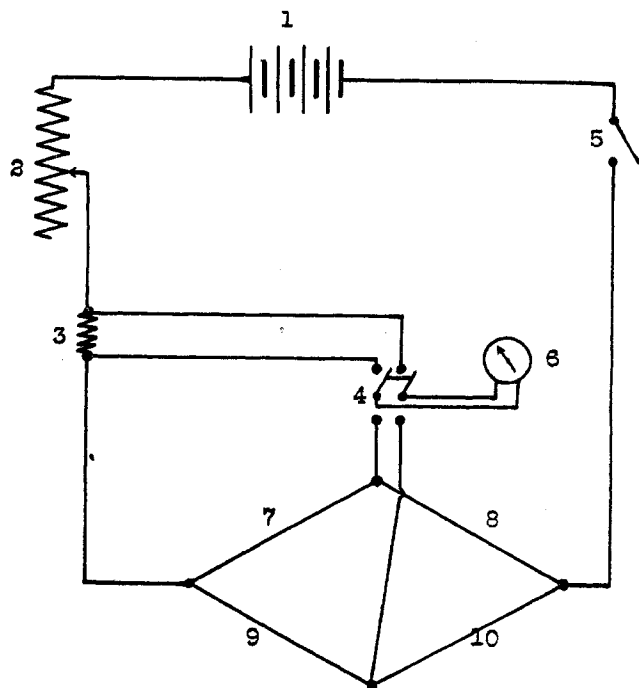

Fig. 1

1—Battery	5—Switch
2—Rheostat	6—Indicator
3—Drop coil (shunt)	7, 10—Wires exposed to gas mixture
4—Double knife, double throw switch	8, 9—Wires exposed to comparison gas

BALANCED BRIDGE ARRANGEMENT—These and other considerations led to the adoption of a balanced bridge arrangement in the method devised at the Bureau of Standards. Two wires, preferably of like material, cross-section, and length, stretched along the axes of two tubes in the same metal block, constitute two arms of a Wheatstone bridge. A Kohlrausch slide wire, such as is used in measurements of the conductivity of electrolytes, together with extension resistances ("end coils") form the other two arms. A portable, inexpensive, d'Arsonval needle galvanometer is used to indicate the balance point. The gas mixture to be analyzed is passed through the tube containing one of the wires; a comparison gas having a constant composition, such as air or hydrogen, and having a thermal conductivity of the same order as that of the gas mixture, or else the residual gas mixture after a constituent has been removed is passed through the tube containing the other wire. The bridge is balanced by moving the contact on the slide wire until the galvanometer gives a zero reading. After the apparatus has been calibrated the position of the contact on the slide wire is an indication of the

relative resistances of the two wires and of the presence and amount of one or more constituents of the gas mixture. Thus, the expensive specially calibrated galvanometer of small range or close scale is in effect replaced by a uniformly divided slide wire of very large range and wide open scale as the measuring instrument.

In order to determine when the current through the bridge just described is correctly adjusted, a second bridge is connected in series. Three arms of this bridge are fixed resistances, and the fourth arm is a wire, exactly similar to the wires of the first bridge, stretched along the axis of a gas-tight metal tube. Since the resistance of this wire constituting the fourth arm varies greatly with small changes of current, the current is adjusted very accurately when the bridge is balanced. By adjusting one of the fixed resistance arms, the bridge may be made to balance with any desired current strength. Both the conductivity apparatus and the current adjustor are placed in an electrically heated oil bath with thermostat. If desired, the same galvanometer may be used for both current adjustment and the conductivity bridge.

When the limit of variation of the desired constituent of a gas mixture is about 10 or 20 per cent, it has been found that by making the extension coils of the slide wire of the proper resistance, the position of the sliding contact with respect to a uniformly divided scale indicates directly and with considerable accuracy the percentages of the constituent when the bridge is adjusted to give no deflection of the galvanometer needle. Consequently the process of calibration consists of determining the values of the resistances which the two bridge extension coils should have for the constituent and gas mixture in question. The calibration of apparatus for the determination of 0–10 per cent carbon dioxide in air will suffice to illustrate a method for finding the value of the end resistances. Fig. 2 shows diagrammatically the arrangement of the apparatus.
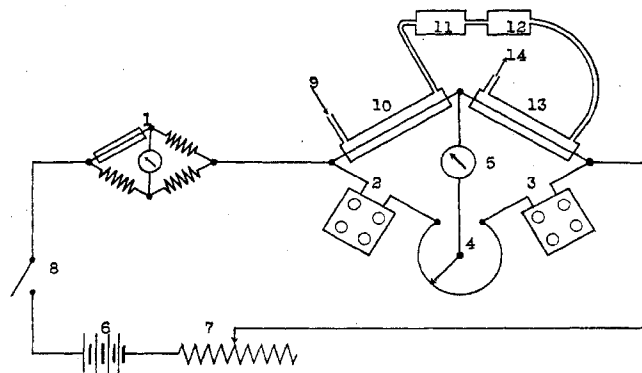

Fig. 2

1—Current adjustment bridge	8—Switch
2,3—Four dial resistance boxes	9—Entrance for gas mixture
4—Slide wire bridge	10, 13—Thermal conductivity cells
5—Galvanometer	11—Carbon dioxide absorber
6—Storage battery	12—Drying tube
7—Rheostat	14—Exit for residual gas

With the contact of the slide wire bridge (4) set at zero, pure, dry air free from carbon dioxide is allowed to flow at a rate of about 20 cc. per minute through

the entrance (9) into the first conductivity cell (10), thence to a carbon dioxide absorber (11), and, after being dried over calcium chloride (12), passes through the second conductivity cell (13) and is discharged at (14). When the gas circuit is thoroughly swept out the switch (8) is closed, the setting of the rheostat (7) is varied until the current adjustment bridge (1) is balanced, and with one resistance box, *e. g.*, (2), set at a definite value, the other resistance box (3) is adjusted until the galvanometer (5) gives no deflection. Care must be taken that the current through the circuit is correct when the final adjustment is made. The settings of the two resistance boxes are noted and by increasing the resistance in (2) by regular steps and obtaining the corresponding values of (3) when the galvanometer (5) gives a zero reading, a series of values of correct end resistances is secured for the lower limit of carbon dioxide content.

A mixture of approximately 10 per cent carbon dioxide–90 per cent air is then prepared in a mercury-sealed gas-holder, carefully analyzed by volumetric apparatus, and then allowed to flow through the gas circuit of the thermal conductivity apparatus as described above for air. With the contact of the slide wire bridge (4) set at the scale division corresponding to the average of the volumetric analyses of carbon dioxide, another series of correct end resistance values for the upper limit of carbon dioxide content is secured.

Choosing the resistances of one box as ordinates and of the other as abscissae, end resistance curves corresponding to the lower and upper limits of carbon dioxide variation are plotted. The intersection of these curves gives the value of the end resistances to be used for this range of variation of the desired constituent in the given gas mixture.

Table II shows two series of end resistance values for a 0–10 per cent carbon dioxide-in-air calibration.

TABLE II—END RESISTANCE VALUES FOR CO_2-IN-AIR CALIBRATION
(Resistance in Ohms)

Box 2	Box 3	
	0 Per cent CO_2	10.28 Per cent CO_2
200	170.6—	174.7
300	270.4+	273.6+
400	370.1	372.45
500	469.9	471.4
600	569.6	570.2—
610	579.55	580.1
620	589.55	589.9
630	599.5+	599.8
640	609.5	609.7
650	619.5+	619.55
660	629.4+	629.4
670	639.4	639.3
680	649.4	649.2
700	669.4	669.05

The curves shown in Fig. 3 are plotted from the end resistance values given in Table II. The excellent agreement between analysis by the thermal conductivity apparatus and by careful volumetric analyses of several carbon dioxide-air mixtures is shown in Table III.

TABLE III—ANALYSES OF CO_2-AIR MIXTURES

AVERAGES OF VOLU-METRIC ANALYSES Per cent CO_2	ANALYSIS BY THERMAL CONDUCTIVITY APPARATUS (Uncorrected Reading of Instrument) Per cent CO_2
0.00	0.20
2.65	2.68
4.85	4.85
7.12	7.14
10.28	10.28

By the use of a suitable switch the same slide wire, galvanometer, and current adjustor may be employed in connection with any desired number of thermal conductivity units. It is only necessary to provide special end resistance coils, which are easily and cheaply constructed, with each of the conductivity units to make the apparatus indicate directly the percentages of the constituents in the various gas mixtures for which the instrument has been calibrated.
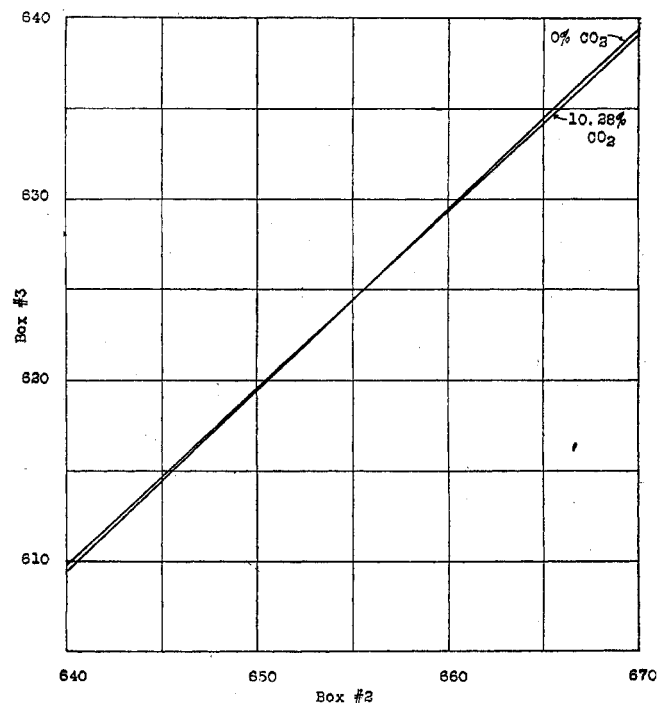

FIG. 3

RECORDER—Unlike the devices used or suggested by others for gas analysis by methods depending upon thermal conductivity, the manually operated arrangement just described may be readily adapted to give a continuous record of gas composition, to actuate plant control mechanism, and to sound an alarm. For these purposes it is only necessary to substitute for the galvanometer and slide wire a recorder of the type manufactured by the Leeds and Northrup Company arranged to adjust automatically the position of a contact on a slide wire until a galvanometer gives no deflection, to draw a curve, or to otherwise provide a record of the position of the contact with respect to the slide wire, and, if desired, to operate mechanical or electrical devices of any suitable construction.

REPRESENTATIVE ANALYSES

In order to indicate the wide applicability of the thermal conductivity method which has been developed and to show the accuracy which has been obtained by its use a series of representative analyses is given below.

HYDROGEN IN HYDROGEN-AIR MIXTURES—The following results were obtained in the calibration of apparatus intended for use in determining the permeability of balloon fabrics to hydrogen. The gas mixture for analysis surrounded one wire of the thermal conductivity apparatus, and pure dry air the other.

TABLE IV—ANALYSES OF HYDROGEN-AIR MIXTURES

ANALYSIS BY GAS INTERFEROMETER Per cent H_2	ANALYSIS BY THERMAL CONDUCTIVITY APPARATUS (Uncorrected Reading of Instrument) Per cent H_2	Analysis from Calibration Curve Per cent H_2
0.096	0.092	0.096
0.150	0.147	0.150
0.207	0.201	0.203
0.204	0.202	0.204
0.231	0.229	0.231
0.278	0.276	0.277
0.406	0.408	0.407
0.556	0.558	0.555
0.704	0.707	0.704
0.846	0.848	0.846
0.962	0.964	0.962
1.175	1.176	1.175

HYDROGEN IN HYDROGEN-NITROGEN MIXTURES—The results given in Table V were obtained on units calibrated for use in the synthetic ammonia plant. The variable gas mixture passed through one thermal conductivity cell and pure hydrogen was used as the comparison gas.

TABLE V—ANALYSES OF HYDROGEN-NITROGEN MIXTURES

AVERAGES OF VOLUMETRIC ANALYSIS Per cent H_2	ANALYSIS BY THERMAL CONDUCTIVITY APPARATUS (Uncorrected Reading of Instrument)					
	Unit No. 6 Per cent H_2	Unit No. 8 Per cent H_2	Unit No. 9 Per cent H_2	Unit No. 11 Per cent H_2	Unit A Per cent H_2	Unit No. 2 Per cent H_2
67.58	67.58	67.58	67.58	67.58	...	...
69.63	69.85	69.88	69.69	69.69	...	...
72.67	72.67	72.67	72.67	72.67	...	...
75.43	75.44	75.52	...	...	75.41	...
74.00	...	...	...	...	74.00	...
71.40	...	...	...	...	71.40	...
66.50	...	...	...	...	66.50	...
42.48	...	...	...	...	...	42.48
44.65	...	...	...	...	...	44.75
47.62	...	...	...	...	...	47.62
...	65.99	65.87	...	...	...	...
...	66.22	66.28	...	...	...	...
...	69.63	69.75	...	...	...	...
...	71.30	71.35	...	...	...	...
...	74.00	73.93	...	...	...	...

NITROGEN IN NITROGEN-HYDROGEN MIXTURES—Table VI shows analyses made by a unit for the synthetic ammonia plant. Pure hydrogen was used as the comparison gas.

TABLE VI—ANALYSES OF NITROGEN-HYDROGEN MIXTURES

AVERAGES OF VOLUMETRIC ANALYSES Per cent N_2	ANALYSIS BY THERMAL CONDUCTIVITY APPARATUS (Uncorrected Reading of Instrument) Per cent N_2
3.43	3.43
5.30	5.35
8.60	8.60

CARBON DIOXIDE IN CARBON DIOXIDE-AIR MIXTURES—Refer to Table III.

CARBON DIOXIDE IN MIXTURES OF HYDROGEN, NITROGEN, AND CARBON DIOXIDE—In Tables VII and VIII are given the results obtained on apparatus

TABLE VII—ANALYSES OF CO$_2$, HYDROGEN, AND NITROGEN MIXTURES (UNIT A)

Hydrogen in Residue Per cent H_2	Nitrogen in Residue Per cent N_2	Averages of Volumetric Analyses Per cent CO_2	Analysis by Thermal Conductivity Apparatus (Uncorrected Reading) Per cent CO_2
40	60	2.42	2.45
40	60	2.53	2.53
40	60	2.79	2.73
40	60	4.55	4.55
40	60	5.30	5.20
40	60	6.90	6.90
40	60	7.69	7.60
40	60	10.05	10.05
37.33	62.67	0.00	0.00
37.33	62.67	1.00	0.90
37.33	62.67	3.29	3.29
37.33	62.67	6.05	6.00
37.33	62.67	8.10	8.27
37.33	62.67	10.03	10.23
29.36	70.64	0.00	0.05
29.36	70.64	2.37	2.30
29.36	70.64	3.67	3.64
29.36	70.64	6.55	6.55
29.36	70.64	10.82	11.07

TABLE VIII—ANALYSES OF CO$_2$, HYDROGEN, AND NITROGEN MIXTURE (UNIT B)

Hydrogen in Residue Per cent H_2	Nitrogen in Residue Per cent N_2	Average of Volumetric Analyses Per cent CO_2	Analysis by Thermal Conductivity Apparatus (Uncorrected Reading) Per cent CO_2
70	30	22.52	22.52
..	..	25.15	25.15
..	..	27.53	27.53
..	..	27.80	27.77

calibrated for the synthetic ammonia plant. The apparatus was arranged in the same manner as that described for the determination of carbon dioxide in air. It is to be noted in Table VII that, though the hydrogen-nitrogen ratio of the mixtures has been varied considerably, the analyses of carbon dioxide by the thermal conductivity method are almost unaffected.

AMMONIA IN MIXTURES OF AMMONIA, NITROGEN, AND HYDROGEN—Ammonia is determined by passing the gas mixture first through one conductivity cell, then through an ammonia absorber, and finally through the second thermal conductivity cell. In Table IX analyses made by two units are given. The residue after the removal of ammonia contained 75 per cent hydrogen and 25 per cent nitrogen.

TABLE IX—ANALYSES OF AMMONIA, NITROGEN, AND HYDROGEN MIXTURES

AVERAGES OF VOLUMETRIC ANALYSES Per cent NH_3	ANALYSIS BY THERMAL CONDUCTIVITY APPARATUS (Uncorrected Readings)	
	Unit No. 10 Per cent NH_3	Unit A Per cent NH_3
0.27	0.39	0.30
2.55	2.52	2.42
2.63	2.65	2.62
5.26	5.20	5.10
5.78	5.63	5.55
8.03	7.96	7.85
8.48	8.36	8.28

HELIUM IN MIXTURES OF HELIUM AND NITROGEN—Helium in mixtures of helium and nitrogen is determined by passing the gas mixture through one thermal conductivity cell while hydrogen is passed through the other cell as a comparison gas. In Table X are shown the uncorrected readings made by a recorder when used in connection with two different thermal conductivity units together with the corresponding analyses made with a gas interferometer.

TABLE X—ANALYSES OF HELIUM-NITROGEN MIXTURES

GAS INTERFEROMETER ANALYSES Per cent He	UNCORRECTED RECORDER READINGS 0–100 Per cent Range		ANALYSES FROM CALIBRATION CURVES	
	Unit No. 1 Per cent He	Unit No. 2 Per cent He	Unit No. 1 Per cent He	Unit No. 2 Per cent He
9.8	7.1	7.5	9.8	10.0
19.8	21.3	22.5	19.8	20.7
30.0	34.3	34.3	30.0	29.9
40.1	45.0	45.7	40.0	40.2
50.3	54.7	55.0	50.3	50.3
58.4	60.9	61.4	58.3	58.4
63.6	64.7	65.0	63.6	63.3
71.8	70.7	71.2	72.4	72.3
82.7	77.2	77.7	82.7	82.7
87.7	80.2	80.7	87.6	87.6
88.8	81.0	81.8	88.9	89.5
90.5	82.0	82.4	90.8	90.5
93.1	83.2	84.0	93.3	93.1
	80–100 Per cent Range			
82.7	81.7	82.8	82.7	82.7
87.7	88.5	89.8	87.7	87.9
88.8	90.0	91.2	88.9	89.0
90.5	91.7	92.7	90.1	90.1
93.1	95.5	96.7	93.1	93.1

Although the direct readings taken from the recorder chart deviate considerably from the corresponding interferometer analyses, the discrepancies disappear

when the direct recorder readings are corrected by means of calibration curves.

CONSTRUCTION OF APPARATUS

THERMAL CONDUCTIVITY UNITS—The thermal conductivity units used in making the representative analyses cited in this paper are a product of evolution. In attempting to eliminate or avoid difficulties encountered in the early forms of construction the present form has resulted. Consequently, though an arrangement has been devised that works surprisingly well, future study will no doubt suggest further improvements.

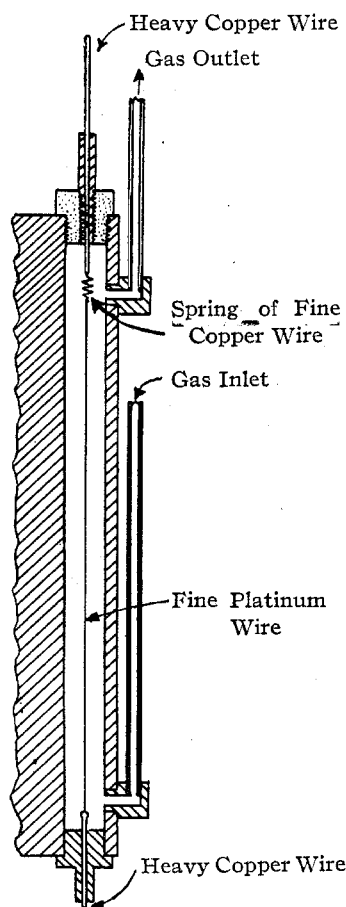In order to secure high sensitivity with a small consumption of energy it has been found that the wires exposed to the gas mixture for analysis and to the comparison gas should preferably be of small diameter and made from metals having a high temperature coefficient of resistance. Wires of nickel, tungsten, and platinum of various diameters and lengths have been successfully employed. Platinum, however, on account of its freedom from reaction with most gases, low thermoelectric power against copper, permanence of physical properties, and the ease of fusing it to supporting and connecting terminals, has been selected as the metal usually most suitable. The best diameter and length to choose for the wires depends upon the current strength to be employed and the sensitivity desired. Wires having diameters of 0.0254 and 0.0508 mm. (0.001 and 0.002 in.) and lengths of 15 and 10 cm. (6 and 4 in.) have given ample sensitivity with bridge currents of 0.15 ampere for the smaller wire and 0.30 ampere for the larger wire. In order to concentrate the resistance in the platinum wires, render the connections to the ends of the wires permanent and the junctions free from objectionable thermal e. m. f., copper wires are fused to each end of the platinum wire. To minimize the danger of the wire being displaced from its position when stretched along the axis of the tube forming the conductivity cell, one copper terminal is made of as heavy a wire as can be conveniently fused to the small platinum wire, and the other copper terminal is made of fine copper wire, which, after one end has been fused to

FIG. 4

Labels on Fig. 4: Heavy Copper Wire; Gas Outlet; Spring of Fine Copper Wire; Gas Inlet; Fine Platinum Wire; Heavy Copper Wire

the small platinum wire, is wound into a helical spring and the free end is soldered to a heavy copper wire.

The gas chambers in which these platinum wires are stretched consist of two tubes in the same metal block, each provided with a gas inlet and outlet and bushings for supporting the wire stretched along the axis.
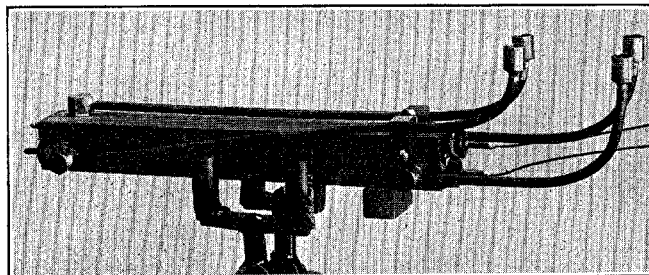
FIG. 5

Brass has been found a suitable metal where non-corrosive gases are used and the tubes are simply cylindrical holes drilled lengthwise through a square brass rod. To minimize the effect on the calibration of any possible displacement of the active wires and to reduce the power required to produce a given temperature difference between the wire and the wall of the tube, the diameter of the tubes or cells is made the maximum permissible. Experiments have shown that when the diameter much exceeds one centimeter convection currents cause unsteady readings. This unsteadiness appears rather suddenly as the diameter of the cell is increased, and the value of the limiting diameter is in somewhat striking agreement with the thickness of the stationary conducting gas film assumed by Langmuir[1] in his discussion of the loss of heat by conduction and convection from a cylindrical surface. Since the electrical arrangement used requires that the wires in the two cells be connected in series, it is necessary to insulate only one end of each wire from the metal block. This insulation is secured by Bakelite bushings screwed into one end of each cell and fitted with brass sleeves to which the wires may be
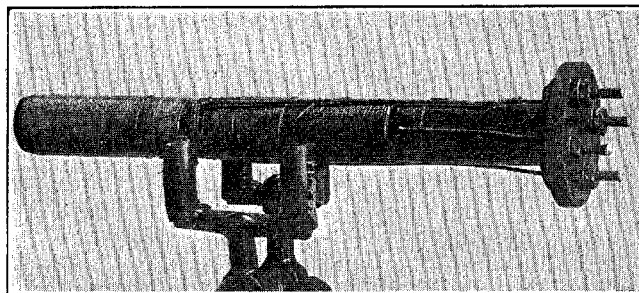
FIG. 6

soldered. The bushings are coated with Khotinsky cement to render the joints gas-tight. Fig. 4 shows a section through one of the cells with the active wire in place and Fig. 5 is a photograph of a complete unit.
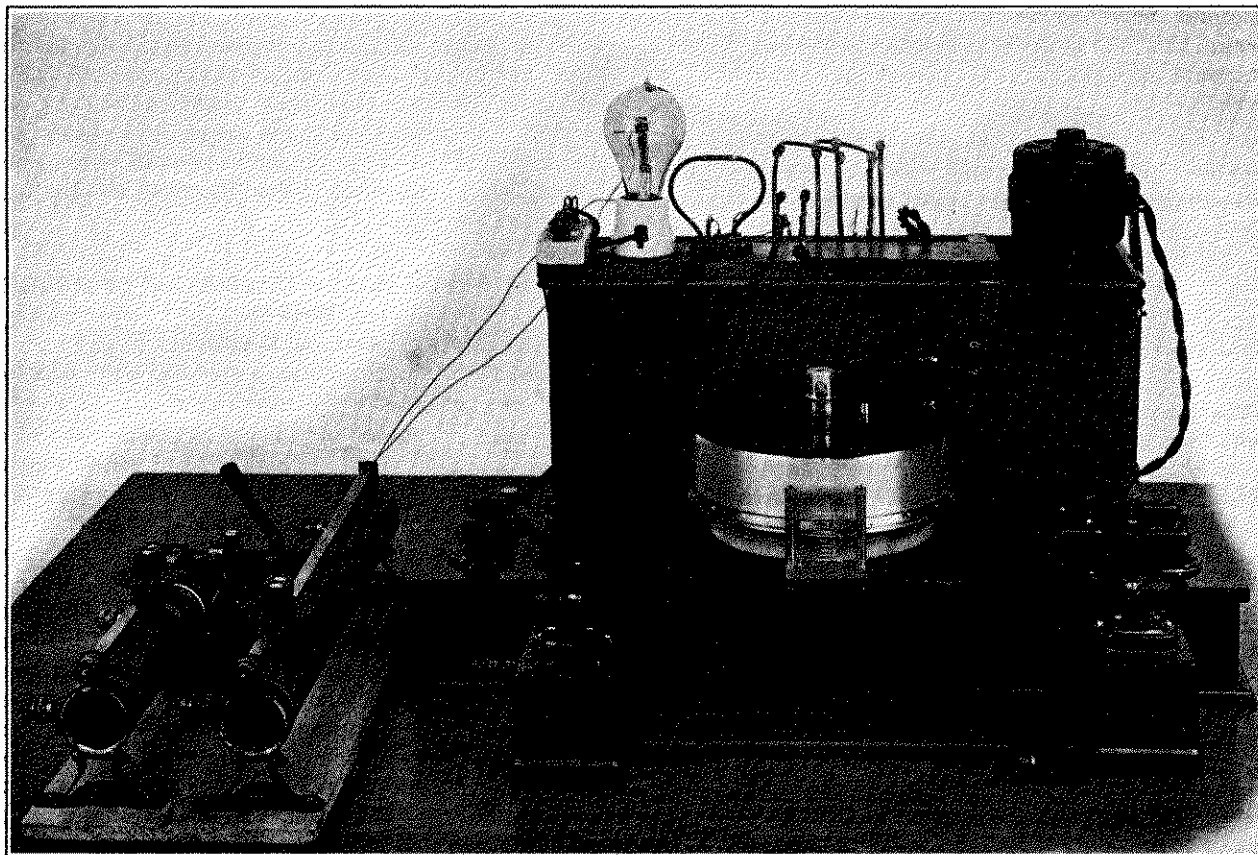
[1] Phys. Rev., 34 (1912), 401.

FIG. 7

END RESISTANCE COILS—After the values of the end resistances to be used with a thermal conductivity unit for the determination of a constituent in a gas mixture have been ascertained, as described in connection with the calibration of apparatus for the determination of carbon dioxide in air, the expensive resistance boxes are replaced by inexpensive coils. These coils are wound non-inductively on bobbins with advance or manganin wire, carefully adjusted to the proper resistances, and mounted for convenience in the oil bath together with the thermal conductivity units. A photograph of such a pair of end resistance coils is shown in Fig. 6.

An idea of the appearance of the manually operated apparatus as set up for experimental work on gas analysis by the thermal conductivity method may be had by inspection of the photograph shown in Fig. 7.

EXTENT OF STUDY OF METHOD AND PLANS FOR FUTURE WORK

Owing to the fact that loss of heat from the active wires in the conductivity cells takes place not only by conduction through the gas, but also to some unknown extent by convection, radiation, conduction through the terminals, and heating the stream of gas flowing past the wire, it has been considered inadvisable and not worth while to attempt to determine the mathematical relations which would make possible the calibration of the apparatus by calculation. Experience has shown that the results obtained by empirical calibration are fully as reliable as those given by the apparatus with which the gas mixtures used in calibration are analyzed.

Although it is known in a general way that the readings are steady and reproducible when the rate of flow of the gas mixtures through the cells does not greatly exceed 20 cc. per minute, a careful study of the quantitative effect of changes in bath temperature and variations in bridge current is yet to be made. Plans for future work include the investigation of these effects, a study of the relative thermal conductivities of various gas mixtures, and further development of a number of devices which have already been applied in a preliminary way to the analysis of more complex gas mixtures than those cited, and to the application of the method to recording and automatic control work.

SUMMARY

1—A new form of apparatus for the continuous analysis of gas mixtures by an electrical method depending upon thermal conductivity is described.

2—Unlike the previous deflection methods of limited application, a balanced-bridge method applicable to the rapid and accurate determination of constituents in a wide variety of gas mixtures of industrial importance has been developed.

3—The adaptability of the apparatus for either manual or automatic recording operation is pointed out.

4—Representative analyses showing the results obtained with apparatus constructed for the determination of hydrogen, nitrogen, carbon dioxide, ammonia, and helium in various gas mixtures are given.

5—The construction of the special forms of apparatus required for this method is described.

6—Plans for future work are outlined.

AN EFFECTIVE CONNECTING BULB
By C. M. Clark
The Chattanooga Chemical Laboratory, Chattanooga, Tenn.
Received November 5, 1919

We have frequent occasion in this laboratory to distil from flasks at a very rapid rate and have many times been troubled by the spray being carried over in spite of the best connecting bulbs we could obtain.
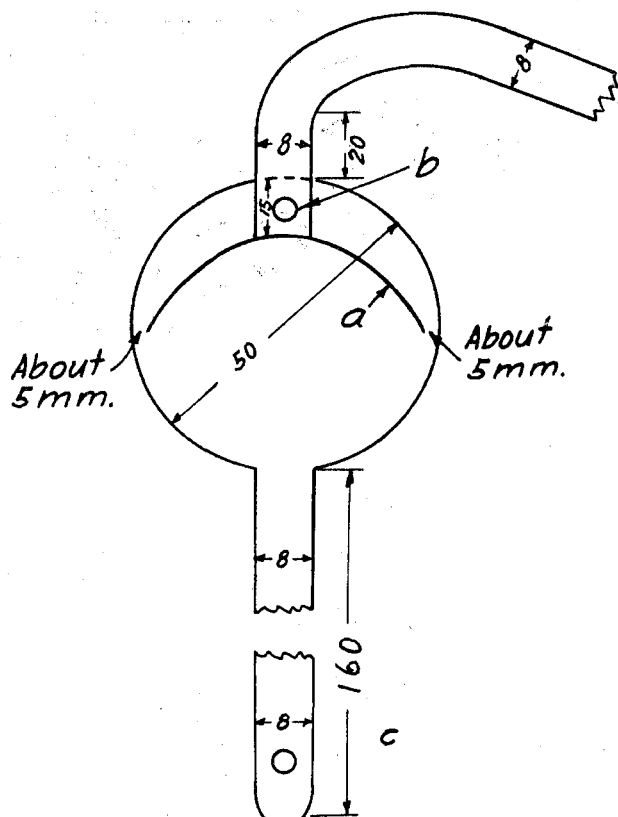
The writer was, in consequence, led to design the bulb herewith illustrated, which has on repeated trials and under the severest conditions fulfilled all requirements. It was first tested by half filling an Erlenmeyer flask with a 10 per cent solution of KOH and catching the distillate in water to which phenolphthalein has been added. Although the boiling was pushed until portions of the liquid were actually carried up into the bulb not a trace of color appeared in the catch water. Under such conditions all other bulbs on the market allowed spray to pass over, coloring the catch water red.

In the figure, *a* is a baffle-plate in the form of a deep watch glass, similar to that used in the "Pistorius" still. It reaches to within about 5 mm. of the sides

of the bulb and effectually prevents any spray from reaching the exit holes *b*. Neither the small hole *c* near the lower extremity of the inlet tube, nor the slight narrowing of the end of that tube is essential, but it is believed that they assist in holding back spray. The dimensions given are in millimeters; they are intended to be only approximate, the general dimensions of the bulb being those of similar bulbs now on the market.

APPARATUS FOR THE DETERMINATION OF MELTING POINTS
By L. M. Dennis
Department of Chemistry, Cornell University, Ithaca, N. Y.
Received November 19, 1919

The most exact method for the determination of the melting point of an organic substance consists in the observation of the melting point and solidifying point of the substance by direct immersion of the thermometer in the partly molten and partly solid mass.[1] This method is, however, frequently impracticable because at least 20 g. of material are necessary for the determination. It has therefore become customary to determine the melting point of an organic substance with approximate accuracy by placing a small amount of the material in a thin-walled glass tube about 1 mm. in diameter, fastening the tube to the side of a thermometer, and heating the thermometer and tube to the temperature at which the sample changes from the solid form to a clear and transparent liquid.

The heating of thermometer and sample tube is usually effected by immersing the two to proper depth in pure, concentrated sulfuric acid and then heating the acid until the melting point of the substance has been reached. It is apparent that if the acid that surrounds the bulb of the thermometer is unevenly heated, the readings may show considerable variation from the true melting point of the substance. For this reason it has been recommended[2] that the temperature be raised very slowly through the last 10°. It is preferable, however, to stir the sulfuric acid while it is being heated, and this can be accomplished either by mechanical stirring with a bent glass rod, or by means of the ingenious device of Olberg[3] in which the heating of the sulfuric acid causes the acid to circulate through the apparatus and thus tends to equalize the temperature throughout the liquid. This tube of Olberg has been simplified by Thiele.[4] The accuracy of a determination of the melting point of a substance with the Thiele tube is largely dependent upon the speed of flow that is set up in the sulfuric acid when the tube is heated. Acceleration of the circulation of the acid will naturally give better results. Very considerable errors that had been made by students in the determinations of the melting points with the Thiele tube seemed to indicate a too slow circulation of the acid.

The Thiele tube is heated at or just below the bend

[1] Lindenbaum, "Die Methoden der Organischen Chemie," I, p. 193.
[2] Wegscheider, *Chem.-Ztg.*, **29** (1905), 1224.
[3] *Repert. anal. Chem.*, **1886**, 95.
[4] *Ber.*, **40** (1907), 996.