of the anodic relation, the cobalt becomes active in acid solution more readily than does nickel.

SEATTLE, WASHINGTON.

THE RAPID DETERMINATION OF CARBON MONOXIDE IN AIR.[1]

By ARTHUR B. LAMB AND ALFRED T. LARSON.

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The breathing of air containing 1% of carbon monoxide by men in moderate activity will lead to loss of consciousness within a few minutes, followed very soon by death. 0.1% of carbon monoxide may cause disablement in about 2 hours and 0.05% is sufficient to induce drowsiness on prolonged breathing.

The testing of the efficiency of gas mask absorbents for carbon monoxide, therefore, involves the precise analysis of air mixtures containing 1% and less of this gas. Moreover, to follow adequately the behavior of an absorbent during a test, frequent and very rapid analyses are required.

When testing of this nature became necessary in the Research Division of Chemical Warfare Service, a search for a satisfactory method was made, but none was found at once sufficiently accurate and rapid for this purpose.

Methods depending upon absorption, such as the cuprous chloride and the Haldane methods, were out of the question, since the volume changes to be measured at these concentrations were so minute. Conversion to carbon dioxide and its determination was not suitable because of the difficulty of securing rapid and at the same time complete absorption of carbon dioxide at very low concentrations. The liberation of iodine from iodine pentoxide furnished a very accurate method, particularly at concentrations of carbon monoxide as low as 0.1%, but it was found to be time consuming.

Thermometric methods depending on the rise of temperature produced by the combustion of the carbon monoxide had, to be sure, been described, particularly in the patent literature, and they had, at least, the merit of rapidity. Thus, Guasco[2] had proposed a differential air thermometer in which one of the bulbs was of platinum covered with platinum black. The device has been found to poison rapidly, requires frequent calibration, and is not accurate at low concentrations.

A. and L. D. Williams[3] had described an arrangement which employs

[2] *Compt. rend.*, **155**, 282 (1912).

[3] U. S. pat. 1,143,473. June, 1915.

an electrically heated catalyst in contact with which the gas burns, the temperature rise being measured by a thermocouple. Unfortunately, the two thermojunctions are separately heated with the result that the accidental temperature differences at the two junctions introduce errors which may completely mask any heating effect resulting from the combustion of small quantities of carbon monoxide.

Phillip and Steele[1] had placed a catalytic material on a wire which was made one side of a Wheatstone bridge, the catalyst being heated by passing a current through the wire. No provision, however, was made to prevent poisoning of the active material; nor is the device sufficiently compensating to detect the small temperature changes resulting from carbon monoxide air mixtures of low concentration.

B. C. Tilghman[2] and H. H. Clark[3] had suggested Wheatstone bridge arrangements in which one side of the bridge is heated to a temperature where combustion of the carbon monoxide takes place. These methods are, however, not truly differential and on that account are of little value for the quantitative measurement of low concentrations of carbon monoxide.

All of the above devices would no doubt be of value in the detection of relatively high concentrations of carbon monoxide, as, for instance, in the operation of signals, warning of the approach to the explosive limit. They would also be undoubtedly rapid in action, but their accuracy would be wholly insufficient for measurements of the low concentrations above mentioned.

Attempts were therefore made to increase the accuracy of the thermometric method without forfeiting its rapidity, and two new modifications of the method were developed which met this requirement. Both measure the temperature rise resulting from the combustion of carbon monoxide in air. In the first method, the combustion takes place in contact with a heated platinum wire, in which case the amount of combustion is constant but not complete. In the second method, combustion takes place in contact with a platinum catalyst and is complete. In the first method, the temperature rise is measured by a Wheatstone bridge arrangement, which is practically a platinum resistance thermometer; in the second, the temperature rise is measured by a thermocouple.

Neither of these methods is an absolute one; that is, both must be calibrated by the use of carbon monoxide air mixtures of known concentrations. As a consequence the absolute accuracy of these methods depends, in part, upon how accurately these concentrations can be determined either by synthesis, or, as was found more convenient in practice,

[1] U. S. pat. 899,068. Sept., 1908.
[2] U. S. pat. 524,361. Aug., 1894.
[3] U. S. pat. 960,823. June, 1910.

by analysis. Since these calibrations are but infrequently required and the analysis of the reference gas can be made at leisure, the method employed for the purpose need not be a rapid one and, therefore, a slow and very accurate method such as the one using iodine pentoxide can be employed. The absolute accuracy of these new methods can therefore be made equal to that of the best chemical method; since in addition they are rapid, they ought to prove useful in many fields.[1]

First Method (Hot Wire Method).[2]

In this method (Fig. 1) the air mixture to be analyzed is passed over a platinum wire heated to a dull red, in contact with which the combusti-
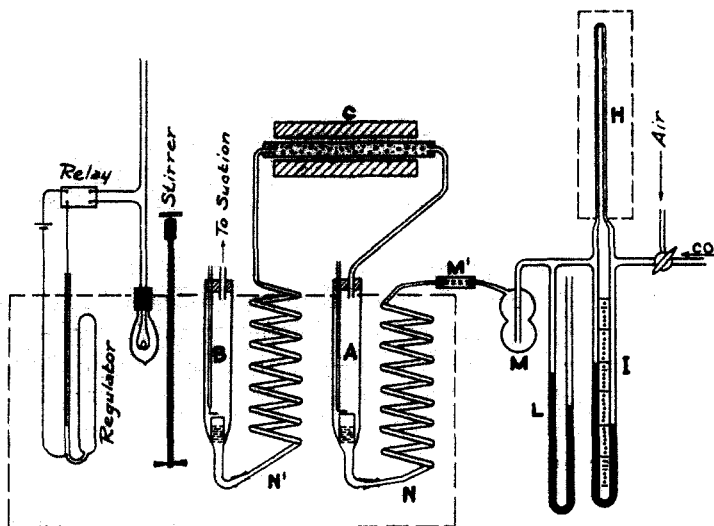

Fig. 1.

[1] U. S. pats. 1,321,063 and 1,321,064 have been granted covering these two methods.

[2] This method finally proved less advantageous for our purposes than the second method (Catalytic Method) to be described later. It was, therefore, not fully developed by us and can doubtless be brought to a much higher state of perfection. Neverthe-less, important details regarding it were worked out; it was put in actual operation, and tests made demonstrated its considerable reliability and accuracy. For this reason a brief description of it and its operation is given.

After our work on this method had been completed a valuable paper bearing on this subject was published by Weaver and Weibel of the Bureau of Standards (Bureau of Standards, *Scientific Paper* **334**, "New Forms of Instruments for Showing the Presence and Amount of Combustible Gas in the Air"). In this paper important fundamental studies are given of the behavior of heated wires in air mixtures containing combustible gases. An apparatus is described for determining combustible gases working on a prin-ciple similar to the above-mentioned First Method. It is not, however, as rigorously differential as this method, in that instead of two identical wires, an active and a coated wire are employed. Moreover, it is not certain from the above paper that this appar-atus, which evidently operated successfully as a detector at the concentrations studied, would at our 10 times lower concentrations operate with the precision required in our analytical work.

ble gas is partially burned, then through a tube of heated copper oxide where the combustion is completed. The gas mixture, free from carbon monoxide, then passes back over a second platinum wire, not only in itself identical with the first wire, but identically mounted and connected in series with it. These two wires constitute two arms of a Wheatstone bridge and after being suitably balanced a change in temperature of either wire with respect to the other will cause a change in relative re·sistance, which is disclosed by a suitable galvanometer. This arrangement, except for the carbon dioxide formed and the slight change in volume, is rigorously differential. To insure identity of temperature in the surroundings and in the gas stream the whole apparatus is submerged in a closely regulated water thermostat, and the gas stream, before reaching the hot wires, is led through long, copper spirals similarly submerged.

The most serious difficulty and one which was underestimated at the outset, was the irregular variation in the relative resistance of the heated wires, even when no carbon monoxide was present in the gas .stream. Thus, these relative resistances were found to vary markedly with changes in the total rate of flow of the gas in spite of apparent substantial identity in the dimensions and shapes of the hot wires and their containers. It was, therefore, necessary to hold the flow carefully constant by means of a sensitive flowmeter. In spite of these precautions large and irregular variations in the relative resistance of the two wires still occurred, so that the effect of the combustion of small concentrations of carbon monoxide on the first wire, was completely masked. The difficulty was finally solved by carefully eliminating eddies in the gas stream. This was accomplished by placing within "P" (Fig. 2) several layers of cotton gauze and covering the end of "P" with a fine-mesh cotton gauze over which the heated platinum wire was directly placed. This gave a steady and apparently stream-line flow and eliminated the marked fluctuations in the relative resistance of the wires.

Fig. 2.

Apparatus.

The apparatus is shown assembled in Fig. 1. The platinum wires ("heaters") are supported within the tubes A and B. C is an electric furnace containing a tube of copper oxide. N and N' are copper tubes wound in a spiral as indicated. H, I, is a flowmeter, the capillary of which is kept in the thermostat. L is a manometer which indicates changes in the pressure of air within the system. M is a wash-bottle for drying the gas while M' is a glass-wool plug which serves to remove acid spray.
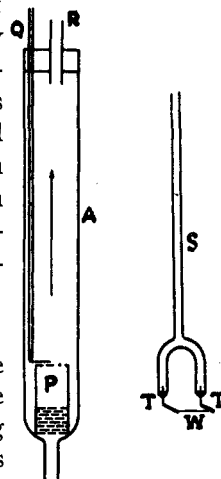
An enlarged view of the heater and its containing tube is shown in Fig. 2. Into the glass fork S are sealed platinum wires (No. 14) which are bent sharply at right angles, the ends being one cm. apart. A slit was cut in the end of each wire and into this was clamped a strand of platinum wire, W, made by twisting together two wires 0.002 inch in diameter. Satisfactory contacts were made by arc welding the ends of the wire to the support. The fork was held rigidly so that the platinum heater fell

TABLE I.—DEFLECTION WITH 0.9976% MIXTURE OF CARBON MONOXIDE IN AIR.

Resistance D = 1100 ohms. E = 900 ohms and F = 77 ohms.
Heating Current = 1.1 amperes.   Galvanometer Resistance = 120 ohms.
Rate of Flow = 1.5 liters per minute.
1000 ohms additional resistance in galvanom-
   eter circuit.

Time.	Galvanometer reading. Cm.	Total deflection. Cm.	Time of adjustment. Min.
9:49 Air	—0.3		
9:58 Air	—0.3		
10:10 Air	—0.1		
10:17 Air	—0.2		
10:18 Gas Mixture	+24.0		
10:19 Gas Mixture	+22.2		
10:20 Gas Mixture	+22.0		
10:22 Gas Mixture	+21.7		
10:23 Gas Mixture	+21.5		
10:27 Gas Mixture	+21.1	21.4	9.5
10:29 Gas Mixture	+21.1		
10:32 Air	+0.7		
10:35 Air	—0.3		
10:42 Air	—0.3		
10:44 Air	—0.2		
10:46 Gas Mixture	+22.5		
10:49 Gas Mixture	+22.5		
10:51 Gas Mixture	+22.3	22.5	6.5
10:53 Gas Mixture	+22.3		
10:55 Air	—0.2		
10:57 Air	—0.3		
11:00 Air	—0.3		
11:03 Gas Mixture	+22.2		
11:05 Gas Mixture	+22.1		
11:07 Gas Mixture	+22.1	22.5	4.5
11:10 Air	—0.7		
11:12 Air	—0.7		
11:15 Air	—0.9		
11:17 Gas Mixture	+22.2		
11:18 Gas Mixture	+22.1	22.9	3.0
11:20 Air	—1.0		
11:23 Air	—1.0		
		22.4 ±0.4	5.7

just over the mouth of P. A storage battery large enough to maintain the wires at a constant, dull red for long periods was used. The current flowing through the bridge was kept constant by means of a slide-wire resistance and a millivoltmeter.

Results.

Results selected from a typical run with a 0.9976% mixture of carbon monoxide in air are given in Table I.

Similar results were obtained with mixtures containing 0.1% carbon monoxide. The percentage reproducibility in both cases was practically identical, being $\pm 2\%$ over an interval of one to two hours, and about 5 minutes was required to reach a definite deflection.

Second Method (Catalytic).

This method depends upon the catalytic combustion of the gas in contact with platinum. At 275–300° this reaction is fast enough so that combustion is complete under ordinary conditions. The temperature rise is measured by means of a thermocouple and galvanometer. After calibration, deflections of the galvanometer represent definite concentrations of carbon monoxide.

This method not only proved to be more accurate than the first method, but also easier to install and operate. It was used for many months in routine testing laboratories of the Chemical Warfare Service, and indeed, made possible the rapid development of carbon monoxide masks and absorbents.

Apparatus.

Two satisfactory types of apparatus were developed, one using a vapor and the other an air bath to heat the gas and the contact mass. The former apparatus is by far the easier to install and it alone will be described in detail in this paper.

A diagram of it is shown in Fig. 3; B was a steel tube 90 cm. long and 7.5 cm. in diameter, closed at one end. The tube was covered except for the upper 25 cm. with several thicknesses of asbestos paper. Boiling diphenylamine was found to give satisfactory results in the vapor bath though it decomposed slowly and had to be renewed from time to time. Sufficient heat to keep the zone of condensation within 30 cm. of the top of tube B was maintained.

The gas mixture to be analyzed was brought to the constant temperature of the vapor bath by a 4 mm. Pyrex glass tube extending to within 5 cm. of the bottom of the vapor jacket, whence it wound backward in a close coil about 15 cm. long and 6 cm. in diameter equivalent to a straight length of about 3 meters. Attached to this coil was the Pyrex glass tube A, 15 mm. in diameter and extending about 30 cm. above the top of the steel tube B. Tube D was fitted into A as indicated. This was made from a length of 4 mm. Pyrex glass tubing to which was attached

a 20 cm. length of 7 mm. tubing, this enlarged portion being constructed as shown in the figure. This tube carried the catalyst and thermoelement shown in the enlarged cross-section given in Fig. 4. The thermocouple was made from No. 30 copper and constantan wires, the joints being welded or silver soldered. (If silver wire had been used instead of copper many of the difficulties resulting from the oxidation of the copper would probably have been avoided.) The distance between the two junctions was about 6 cm., this portion of the element being made of the constantan wire. The copper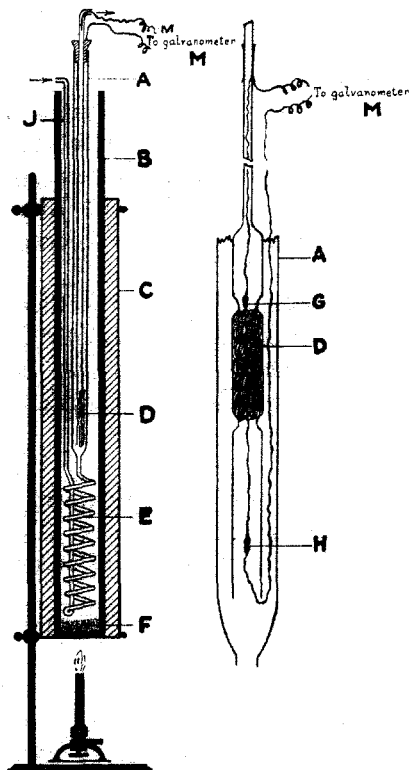 leads extended through the rubber connections and were attached to a galvanometer. A wall type d'Arsonval galvanometer, having a resistance of approximately 120 ohms and giving a deflection of about 0.30 cm. per microvolt on a curved scale 50 cm. from the galvanometer mirror, was used in this work.

Catalyst.

Catalysts were made, some from platinum wire, 0.05 mm. in diameter, and others from platinum gauze, woven from a similar wire. When the wire was used, it was wound into the form of a 2 mm. spiral and then pressed into a fairly compact mass. One gram of this wire gave sufficient surface for our purpose. To prepare it the platinum was first cleaned with acid and then covered with platinum black by electroplating in a solution of chloroplatinic acid in the usual manner. When a heavy coating had been deposited, the wire was washed and then electrolyzed, first in dil. sodium hydroxide solution and then in dil. sulfuric acid, during which time the current was commutated as in the previous plating. This operation was found to be absolutely essential to the successful preparation of the catalyst. The catalyst was now washed and dried and placed in tube D, as shown in Fig. 4. Junction G lay near the upper surface of the catalyst and was as centrally located within the tube as possible. The catalyst was firmly packed into the tube so as to insure firm lodgment and to prevent channels through which the gas might pass without coming in contact with the catalyst.

Fig. 3.   Fig. 4.

This method could, of course, easily be made into a continuous recording one by the use of various electrical recording devices now in the market.

Calibration.

The apparatus was calibrated by passing through it air containing known percentages of carbon monoxide. Because variable rates of flow produce variable galvanometer deflections, it was necessary to maintain a fixed rate of flow, which rate was governed by the nature of the testing to be done. The number of points to be determined for purposes of calibration was also governed largely by a similar consideration.[1]

To fix a given point, a certain concentration of gas was drawn through the machine until the galvanometer readings became constant. Two samples of the gas were then withdrawn and analyzed by the iodine pentoxide method. The concentration was now altered and a second point obtained, and so on, for as many points as seemed desirable. As an illustration, the results obtained in the calibration of an electrically heated apparatus (Unit No. 2, New Interior Building Laboratory) are given in Table II.

TABLE II.—CALIBRATION.

Galvanometer deflection.

CO in air mixture. %.	Observed. Cm.	Computed from empirical formula. Cm.	Deviation from empirical formula.	
			Cm.	% total air.
0.057	4.5	4.75	—0.25	—0.003
0.104	8.8	8.70	+0.10	+0.001
0.264	22.8	22.73	+0.07	+0.001
0.441	39.0	39.16	—0.16	—0.002
0.706	(66.0)[a]	65.61	+0.39	+0.004
1.127	(111.8)[a]	112.09	—0.29	—0.003
			±0.21	±0.002

[a] In these measurements additional resistance had to be inserted in the galvanometer circuit.

These results are represented graphically by the solid curve in Fig. 5. The observed deflections are represented by the empirical equation $D = 82(\%) + 15.5(\%)^2$ with an average deviation of only 2 mm.

It is of interest to compare the above observations with what would be expected had none of the heat of combustion been lost to the surroundings. In this computation the specific heat of air is taken as 0.237 at 275–300°, the molecular heat of combustion of carbon monoxide as 68040 calories, the temperature coefficient of e. m. f. as 57.03 microvolts per degree and the apparent molecular weight of air as 28.8. The galvanom-

[1] In the testing of absorbents for CO, a 1% CO air mixture has generally been used, although 0.5% and 0.25% have been found desirable at times. The "break" in the absorbent was usually taken as the point at which 0.1% CO leaked through. These points on the galvanometer scale are therefore of considerable interest and it is important that CO air mixtures of about these concentrations be used in the calibration.

eter showed a deflection of 0.0323 cm. per microvolt of 1.84 cm. per degree. This would then require a deflection of 183.6 cm. for a 1% carbon monoxide air mixture, corresponding to a temperature rise of 99.66°. This value has been used to draw the dotted line in Fig. 5, representing the calculated deflections for different concentrations of carbon monoxide.
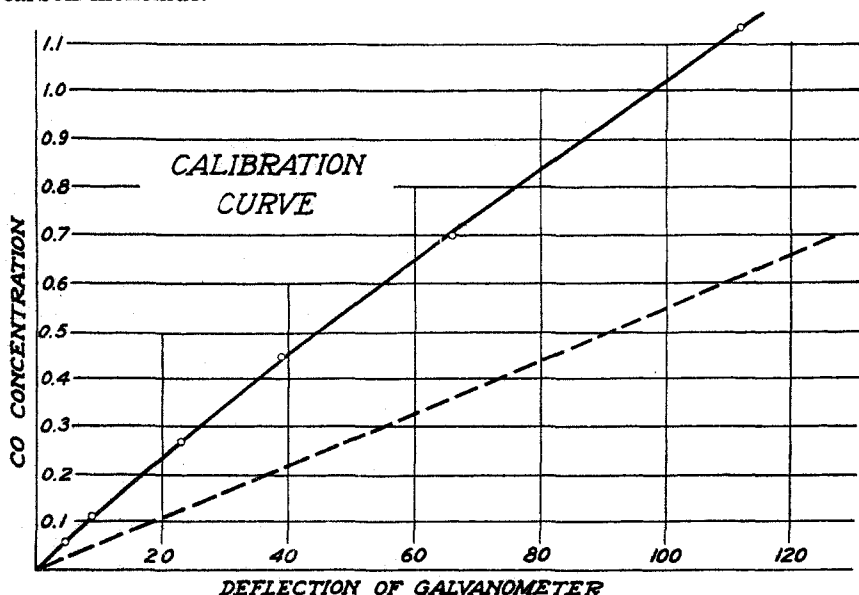

Fig. 5.

The observed deflections for this apparatus are about half that calculated on this basis, showing that a very considerable dissipation of heat occurs. The gradual inflection of the curve representing the observed results indicating a lesser relative heat loss for higher concentrations and higher temperatures is interesting and is probably explained by the fact that at the higher temperatures a great increase in the reaction velocity occurs so that the reaction zone in the contact mass becomes smaller and hence the loss of heat by conduction less.

Longevity of Catalyst.

The successful operation of this device depends upon the permanence of the platinum catalyst. Anything which will change the character of the platinum black surface will impair and in some cases completely destroy its catalytic properties. A high temperature, for instance, will change the platinum black to a grey, which is considerably less active than the black. It was therefore important not only that there should be sufficient platinum to complete the combustion of the carbon monoxide present, but also that this surface should be in such excess that the

heat generated per unit area of its surface was not great enough to effect the conversion to the grey variety.

The introduction of halogens into the gas stream produces permanent poisoning of the catalyst. When this occurs the catalyst must be removed from the apparatus and washed in hot nitric acid or even replated in some cases in order to bring it back to its former activity. Sulfur compounds were also injurious to the contact surface, but in such cases drawing pure air through the heated catalyst frequently restored it to its former effectiveness. The effect of sulfur dioxide on the catalyst is shown in the following table:

TABLE III.—EFFECT OF SULFUR DIOXIDE ON CATALYST.

Concentration of CO, approx. 0.2%. Temperature of air bath, 300°. Unit No. Ia.

Time.	Gal. deflection. Cm.
5:20	25.3
SO₂ introduced 1 part per 100,000 (by volume)	
5:23	24.6
5:26	23.3
5:30	23.1
5:35	22.6
5:40	21.9
5:45	21.2
5:50	20.5
5:55	19.8
6:00	19.1
6:05	18.4
6:10	17.7
6:15	17.0
6:16 SO₂ off.	
6:17	19.0
6:19	19.6
6:30	19.6

It will be noted that the rate of "fatigue" is proportional to the time, being 0.7 cm. for each 5-minute interval. When the sulfur dioxide was turned off, the galvanometer deflection increased and finally reached a constant value, though one lower than at the outset. If the temperature be raised to 350° and air passed at the same time, this poisoning effect can be entirely removed.

A few of the most frequent sources of halogens and sulfur compounds which were encountered and which must be guarded against deserve mention. When carbon dioxide is made by the dehydration of formic acid, the conc. sulfuric acid used suffers slight decomposition into sulfur dioxide. Again, when the gas is dried by *bubbling* through conc. sulfuric acid enough acid spray is carried along with the gas to give trouble. Rubber connections made from fresh, cold-cured rubber give off sulfur chloride and must be heated in strong alkali before use. The air with which the

carbon monoxide is being diluted often causes trouble. It was found advisable to draw the air from out of doors, in order to eliminate every possibility of contamination. Some absorbents give off gases which produce poisoning effect, in which case provision has to be made for their removal.

When precautions were taken to avoid these rather patent sources of contamination no difficulties were experienced. The same catalyst mass was often employed almost continuously for many weeks without replacement. It is advisable, however, when a machine is in constant use, to check its reading against a reference gas once a day, or better still, before and after prolonged series of tests. Any slight poisoning of the catalyst would then be disclosed and correction for it could be made.

Accuracy of Catalytic Method.

An estimate of the accuracy of this method can be gained from the close agreement of the observed galvanometer deflections obtained with

TABLE IV.—REPRODUCIBILITY OF DEFLECTION WITH 0.1% CO AIR MIXTURE.

Concentration of CO = 0.117% (by volume).
Rate of flow   = 1.47 liters per minute.
Temperature of bath = 275°.

Time. Min.		Galv. deflection. Cm.	
0	air	0.3	
1	0.1% CO	10.5	
3		12.1	
5		12.3	12.3[a]
6		12.4	
7		12.5	
8		12.6	
10	air	0.7	
14		0.5	
16		0.3	
19		0.3	
21	0.1% CO	12.3	12.3
22		12.4	
24		12.6	
25		12.6	
26		12.6	
30	air	0.4	
33		0.3	
35	0.1% CO	12.0	
36		12.5	12.3
37		12.6	
38		12.6	
41	air	0.5	
44		0.3	

[a] When these values are referred to the calibration curve (Fig. 4) it will be noted that the galvanometer deflections are greater than one would expect for gas of this concentration. The pure carbon monoxide used in this test had been kept in a galvanized tank for sometime and the high reading is no doubt due to the added heat of combustion of the hydrogen which had accumulated in the tank.

different concentrations of carbon monoxide in calibrating an apparatus, for instance No 11*a*, with the empirical formula $D = 85(\%) + 15.5(\%)^2$, characteristic of it. As can be seen from Table III, the average percentage deviation here from the formula was $\pm 0.002\%$, over the whole range, based on the air.

The reproducibility of the readings is shown by the following table (Table IV) where observations made when air and a 0.1% carbon monoxide mixture were alternately drawn through the machine are recorded.

It is evident that over this interval the galvanometer readings are reproducible to within a millimeter, or to within 1%; this corresponds to an absolute reproducibility in this mixture of 0.001% carbon monoxide based on the total air.

The reliability of this device in the estimation of carbon monoxide is further shown by the results tabulated below. This table (Table V)

TABLE V.—COMPARATIVE EFFICIENCIES.

Carbon Monoxide Canister. A—Thermometric Method. B—Iodine Pentoxide
Method. Against 1% CO Air Mixture.

Canister No. 20.

Mins.	5.	45.	120.	165.	195.	235.	248.
% Leakage by A	0.2	0.3	0.5	1.0	1.5	4.8	10.0
% Leakage by B	0.5	1.0	1.1	1.2	2.1	4.7	11.7
% B — % A	—0.3	—0.7	—0.6	—0.1	—0.6	—0.1	—1.7

Canister No. 21.

Mins.	5.	45.	120.	165.	200.	230.	254.
% Leakage by A	0.2	0.1	0.3	0.5	2.4	5.1	9.7
% Leakage by B	0.3	0.0	0.6	0.6	2.5	5.0	10.5
% B — % A	—0.1	0.1	—0.3	—0.1	—0.1	0.1	—0.8

Canister No. 22.

Mins.	5.	45.	120.	156.	170.	180.	
% Leakage by A	0.3	1.1	1.7	5.3	9.8	15.7	...
% Leakage by B	0.8	1.4	1.8	5.7	10.7	16.1	...
% B — % A	—0.5	—0.3	—0.1	—0.4	—0.9	—0.3	...

Canister No. 23.

Mins.	5.	45.	120.	165.	176.	183.	
% Leakage by A	0.1	0.4	0.8	5.0	10.3	15.3	...
% Leakage by B	0.0	0.0	0.5	4.6	8.9	15.5	...
% B — % A	0.1	0.4	0.2	0.4	1.4	—0.2	...

Canister No. 24.

Mins.	5.	45.	120.	165.	184.	200.	215.
% Leakage by A	0.0	0.1	0.2	1.4	4.9	9.8	15.0
% Leakage by B	0.0	0.0	0.0	1.1	4.8	10.5	15.3
% B — % A	0.0	0.1	0.2	0.3	0.1	—0.7	—0.3

Canister No. 25.

Mins.	45.	120.	150.	190.	211.		
% Leakage by A	0.4	1.2	3.0	9.6	14.7	...	...
% Leakage by B	0.8	1.1	4.6	10.3	14.5	...	...
% B — % A	—0.4	0.1	0.4	—0.7	0.2	...	...

contains the results of a series of carbon monoxide canister tests in which the iodine pentoxide method and this thermometric method were both used in testing the effluent gases. At every point where an analysis was made by the chemical method a similar analysis was made by the thermometric device. The fine agreement of the two methods shows the new one to be entirely trustworthy.

Assuming for the moment that the values obtained by the iodine pentoxide method are correct, the average discrepancy of the above results by the thermometric method is only 0.38%. At first glance this might appear to be a large average where such small quantities (0.2%–10.0%) are concerned, but when it is remembered that the tests are made on a 1% gas and that, therefore, this percentage variation corresponds only to an error of 0.0038% on the total air mixture, it will be recognized that this represents a very excellent agreement. This agreement is especially satisfactory when it is remembered that the results were secured in routine runs made under the stress of war·time demands.

Actually, since the thermometric method was calibrated by means of iodine pentoxide, the above discrepancies are essentially accidental, and should not all be charged to the thermometric method. In other words, the real discrepancies are presumably somewhat less than 0.0038%.

Summarizing our observations regarding the accuracy of this catalytic method (Method No. 2), we would say that at least on mixtures of 0.1 to 1% of carbon monoxide the method can reasonably be relied upon for an accuracy of ±0.003%, based on the total air.

Summary.

1. The necessity for an accurate and rapid method for the analysis of dilute carbon monoxide air mixtures in the study of gas mask absorbents for carbon monoxide has been explained.

2. Two thermometric methods answering this requirement have been described. In the first method the gas mixture is passed over a platinum wire heated to redness and the carbon monoxide is partially burned in contact with it. The gas mixture is then freed of carbon monoxide by passing through heated copper oxide and is brought back in a thermostat over another identical platinum wire heated by the same electric current. The first wire is the hotter because of the combustion which occurs on it— and the resultant relative change in the resistance of the two wires serves as a measure of the concentration of the carbon monoxide. In the second method the mixture is passed through a platinized, platinum catalyst when the carbon monoxide is completely burnt. The temperature rise is measured by a thermoelement and indicates the concentrations of the carbon monoxide.

3. Both methods are rapid. The latter is particularly accurate, easy to install and to operate. With reasonable precautions the activity of

its catalyst remains constant so that machines have been in constant satisfactory operation for many weeks at a time. Being very nearly instantaneous these methods are particularly useful for continuous analysis of a changing gas mixture. Attempts to apply them to the analysis of flue and combustion gases are already under way.

WASHINGTON, D. C.

STUDIES IN CONDUCTIVITY. VI. THE BEHAVIOR OF MIXTURES OF TWO SALTS CONTAINING A COMMON ION IN ANHYDROUS FORMIC ACID SOLUTION.

BY H. I. SCHLESINGER AND F. H. REED.[1]

The first 4 papers of this series[2] have dealt with the agreement of solutions of formates in anhydrous formic acid with the demands of the law of mass action, when the degree of ionization is determined by the conductivity method, although in such solutions these electrolytes are very highly ionized. Since highly ionized substances in other solvents do not obey this law, there exist at present no measurements for strong electrolytes which can be used to verify the deductions which are made from the law for the behavior of mixtures of two electrolytes with a common ion. An investigation of such mixtures therefore seemed desirable, especially as agreement with the law in the behavior of the mixtures, as well as of the individual salts, would dispose of the possibility that the agreement in the case of the latter is due to any accidental cancellation of deviations.[3] This study, in addition to having fulfilled the purposes just mentioned, has resulted in bringing out some points that may lead to a better under· standing of concentrated solutions and has thrown further light on the peculiar behavior of the formates of the alkaline earths.

In most details the methods of Schlesinger and Martin were followed without change except for the following points: The formic acid was prepared by distilling Baker & Adamson's acid, prepared especially for our work, from $1/10$ its volume of phosphorus pentoxide at $20°$ to $27°$, and a pressure of 10 to 18 mm. Three distillations, in the apparatus already described, usually produced an acid with a specific conductivity

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[1] The work reported in this and the preceding paper of this series has been pre· sented to the Faculty of the Ogden Graduate School of Science of the University of Chicago by F. H. Reed in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was completed in June, 1917.

[2] Schlesinger and collaborators as follows: With Calvert, THIS JOURNAL, 33, 1924 (1911); with Martin, Ibid., 36, 1589 (1914); with Coleman, Ibid., 38, 271 (1916); with Mullinix, Ibid., 41, 72 (1919).

[3] See also the seventh paper of the series which follows.