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AN APPARATUS FOR CONTINUOUS GAS ANALYSIS

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The apparatus herein described is designed to afford a continuous determination of moderate concentrations of a given constituent in a flowing gas mixture, and to register the concentration automatically by electrical means. The principle is to scrub a definite proportion of the gas with a definite proportion of a suitable absorbent and to determine the titer of the resulting solution by measuring its electrical conductivity.

Apparatus

From a large reservoir R (Fig. 1) the absorbent is fed slowly through a tube terminating in a small bore capillary A[1] of 7 mm. outside diameter, whose flat, fine-edged tip[2] is horizontally disposed. The rate of flow is maintained fairly constant by means of the constant level device S, so that the liquid falls from the tip of the capillary in drops of uniform volume at intervals of about eight seconds.[3] Each drop falls freely through the bulb B upon the aperture C, forming a thick film which traps the gas in the tube CD, of about 4 mm. bore, and forces it along in descending by gravity to the gooseneck at D. The latter is a capillary constriction of about 1.5 mm. bore, suitably bent so as to arrest each droplet until it is displaced by the impact of the succeeding drop.[4] From this it results that the same volume of gas, namely, the volume of the tube between the points G and D, is aspirated by each drop of the liquid.

The temperature is kept constant by immersion in a thermostatic bath contained in the receptacle U, so that the quantity of gas in each sample is assumed to vary only with the barometric pressure. The gas is introduced at N at a rate slightly in excess of that at which it is being drawn through the coil O by the pump action, the overflow escaping through the side arm P of sufficient length to prevent air from entering the coil. All of these tubes should be of sufficient bore to afford an easy flow of gas.

After having been thus brought into contact in a definite proportion by volume, the liquid and the gas traverse the coiled tube E, which should be long enough to insure practically complete absorption of the desired constituent of the gas. They are separated at the widened lower end F of the coil, where the films are disrupted and the liquid flows into the cell GIJ, the spent gas escaping through the tube Q. The overflow from the cell passes out through the siphon L, the outer arm of which is bent upward at its lower end, the tip M being level with a point just above the electrode H.

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[1] A bore of about 1 mm. is adequate and the length of the capillary is selected so as to give the desired rate of flow when the liquid is under a pressure head equal to that maintained by the constant level device.

[2] The fine edge may be obtained by grinding the tip in a Wood's metal sleeve, as described by Harkins and Brown, THIS JOURNAL, **41**, 499 (1919), and later by Whitman, Young and Wang, *Ind. Eng. Chem.*, **18**, 363 (1926).

[3] At this rate of formation the size of the drop varies by less than 0.3% for a difference of one second in its time of formation; see Whitman and others, ref. 2. A more rapid rate could be used if desired, since the constant level device is capable of maintaining a high degree of uniformity.

[4] No great difficulty is inherent in the correct adjustment of the goose-neck, whose shape can be altered by bending the softened glass until found satisfactory by trial.

In the cell illustrated, the tube I, having an internal diameter of about 2 mm., is bent upward at the ends so as to prevent small gas bubbles from collecting in it. The electrode compartments G and J are similar in shape to an oblique cone, and the electrodes H and K are disks of platinized platinum, each of which is welded to a stout platinum wire about an inch in length. A portion of this wire is imbedded in a glass knob sealed to the wall of the vessel and the upper end is attached to a finer wire leading out of the apparatus. The wire leading through the siphon tube L is of platinum and requires a gas tight seal at V where it emerges. The dimensions and shape of the cell are designed to afford rapid and complete flushing, so as to diminish the time lag attending changes in the composition of the solution.

The long, narrow tube I permits the determination of the conductivity by a method using direct current and possessing the advantages of rapidity and adaptability to recording instruments. This method requires a cell resistance of the order of 10^5 ohms. The cell is connected in series with a low resistance galvanometer in a direct current circuit of about 100 volts, in which the potential is constant or readily adjustable. For this purpose radio "B" batteries have been found very serviceable, if the circuit is closed only for brief intervals. Fig. 2 illustrates an arrangement for detecting and compensating any slight changes in the voltage of the "B" battery. Here the current that flows through a standard fixed resistor, of about the same resistance as that of the cell, is made a measure of the potential and the latter is capable of minor adjustment by means of a variable potential unit, consisting of a 1.5-volt dry cell around which is shunted a rheostat of about 200 ohms. With this arrangement the conductivity of the solution may be assumed to be directly proportional to the current, since variations of the polarization at the electrodes will be only a negligible fraction of the applied voltage, and the total resistance of the circuit will not differ appreciably from that of the cell alone. With a current of about one milliampere the effect of electrolysis is scarcely perceptible.

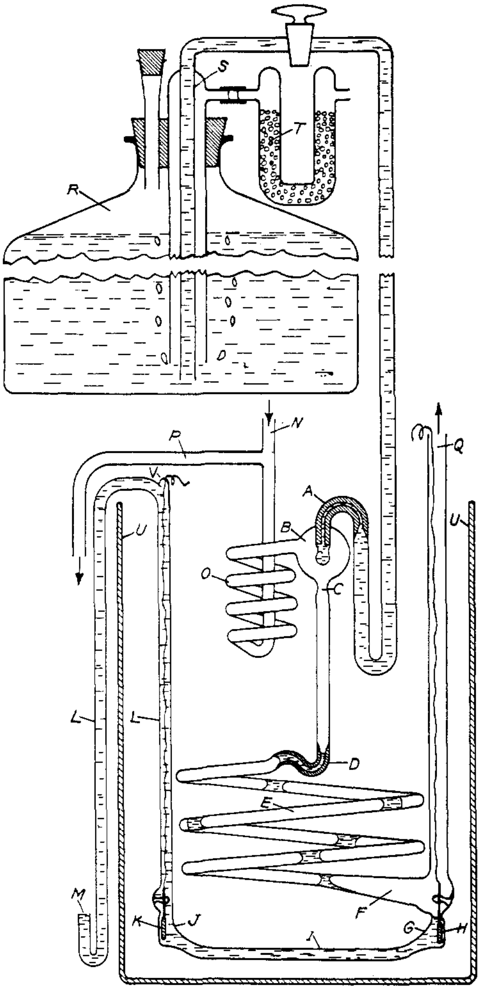

Fig. 1.

If a recording instrument is used in place of the simple galvanometer, its timing mechanism should be made to close the circuit a few seconds before registering and open it immediately afterward. An instrument of the self-balancing potentiometer type, such as a Leeds and Northrup recording pyrometer, would have to be shunted with a suitable fixed resistance and might require modification of its range by altering the zero offset.

Calibration

Method I.—An empirical calibration of the apparatus can be obtained by operating with gas mixtures of known composition, and plotting these compositions against the corresponding conductivities observed for the resulting solutions. This method is perhaps preferable for mixtures with a fairly high content, say 5% and above, of the gas sought, or in cases where absorption is incomplete.

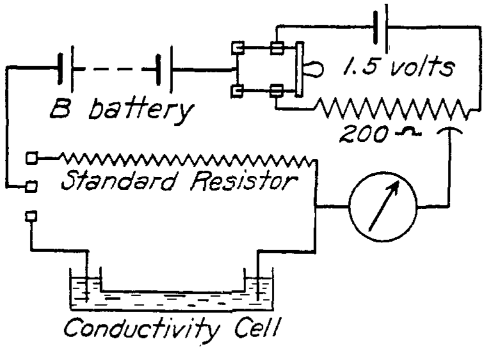

Fig. 2.

Method II.—If the apparatus is to be used for low concentrations of a readily absorbed gas, it is possible to derive a calibration curve where conductance data are available. This second method consists in making careful determinations of the liquid drop size, which will be referred to as *a*, and of the capacity of the cylinder CD, which will be referred to as *b*. The former measurement may be obtained by collecting the liquid that overflows at M resulting from the fall of a counted large number of drops during operation at a steady state. The determination of *b* is best made under similar conditions, using an inert gas and measuring the quantity delivered from the tube Q. If this gas is collected by water displacement, a little care is necessary in order to maintain the pressure at the exit exactly equal to that at the intake, namely, barometric; for otherwise the apparatus will not function properly.

If, during the fall of n drops, an observed volume V cm.^{3} has been collected over water at the room temperature T_r, under barometric pressure P and saturated vapor pressure p_r, while T and p are, respectively, the thermostat temperature and the corresponding aqueous vapor pressure in the tube CD, the capacity b may be calculated as follows:

$$b = \frac{VT(P - p_r)}{nT_r(P - p)} \text{ cm.}^3$$

Although b is a constant for the apparatus, the number of moles m of dry gas aspirated by each drop will vary, of course, with barometric pressure. Assuming perfect gases and expressing pressures in mm. of mercury, the value of m would be

$$m = 273(P - p)b/22{,}420 \times 760\ T = 1.602 \times 10^{-5}(P - p)b/T.$$

From the values thus obtained for a and m it is a simple matter to calculate the relationship of the gas composition to the concentration of the resulting solution, and hence to the conductivity of the latter as computed from conductance data. An example will be given in a later section. In regard to this method of calibration, which is capable of great accuracy for concentrations less than 2%, it must be admitted that it does not take into account the quantity of gas absorbed by a liquid drop before the latter reaches the goose-neck D.[5]

Applications

For gases such as NH_3, HCl or SO_2, the most convenient absorbent would be distilled water, provided the other gases in the mixture are not very soluble. The conductivity of the water, which may be negligible but can be tested from time to time, will then correspond to zero gas concentration. With the aid of conductance data and a single determination of the cell constant, a calibration curve for low concentrations may be obtained by Method II.

For gases requiring chemical absorption, for example, Cl_2, H_2S or CO_2, a carefully standardized reagent is required and the range of the apparatus is limited by the concentration of the reagent, if the upper limit is to be represented by complete neutralization of the solution. An absorbent should be chosen which does not yield a precipitate. In such cases the zero point corresponds to the conductivity of the unchanged solution; and the maximum gas concentration capable of absorption, as calculated from the known titer of the reagent and the apparatus constants a and b, corresponds to the conductivity of the equivalent salt solution at neutrality. According to the theoretical considerations discussed in a later paragraph, the intermediate concentrations should fall on a straight line when plotted against conductivity.

Adaptation for the Determination of Carbon Monoxide

The apparatus has been used successfully for the determination of small concentrations of carbon monoxide in the presence of hydrogen, methane and other gases.

After the removal of any carbon dioxide that may be present, the gas is passed through a tube containing iodine pentoxide at 140 to 150°, where the carbon monoxide is preferentially oxidized with the liberation of iodine. Vapors of the latter are removed in a tower of moist potassium iodide crystals, and the residual gas is analyzed for carbon dioxide in the apparatus illustrated, using a standard solution of carbonate-free potassium hydroxide as the absorbent.

A stock of 0.5 *N* potassium hydroxide was prepared in the following manner. To a 4% solution of c. p. caustic potash in which the carbonate content had been determined, the theoretical quantity of barium hydroxide was added to precipitate the

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[5] It can be shown that, even if absorption were complete in this brief interval of time, the calculated value of the mole fraction would exceed the actual value C only by the quantity $C^2 + C^3 + C^4 + \ldots$, which is relatively small when $C < 0.02$.

carbonate. After the latter had settled, the solution was decanted and made up with freshly distilled water to exactly 0.5 N as standardized against benzoic acid, precaution being taken to prevent contact with air containing carbon dioxide. This stock solution was stored in a paraffin lined, tightly stoppered bottle. By means of a large pipet, of about 800 cm.^{3} capacity, a portion of the stock solution was transferred to the reservoir R, and then diluted with freshly distilled water measured from the same pipet. For use in determining carbon dioxide concentrations up to 2%, a supply of about 16 liters of an exactly 0.025 N potassium hydroxide solution was thus prepared from time to time without the necessity of repeated purifications and standardizations.

Referring to the diagram, Fig. 1, it will be seen that by connecting the tube P with the tube Q, for example with rubber tubing, the gas in the system will be caused to circulate through the apparatus, so that it will be purged and become inert toward the hydroxide solution. Eventually a pure sample of the latter will fill the cell and a determination of its conductivity can be made at the outset and also whenever desirable later. With the aid of this determination in addition to the measurements of the apparatus constants a and b, as indicated under Method II, the calibration of a particular apparatus was obtained at 25°, and it will be given here as an illustration.

Since the determinations of the conductivities, here indicated by k, were made by measuring the direct current flowing through the cell under a fixed voltage, which in this case was 92.5 volts, the values of k for the sake of simplicity will be given in milliamperes. The observed value of k for 0.025 N potassium hydroxide was $k_o = 1.440$ milliamperes. The equivalent conductances at 25° of potassium hydroxide and $^1/_2$ K_2CO_3 at 0.025 N, as derived from the data of Kohlrausch, were found to be 253 and 126, respectively. Hence the milliampere reading corresponding to 0.025 N K_2CO_3 should be $k_n = 1.440 \times 126/253 = 0.717$ milliamperes.

Readings corresponding to intermediate mixtures of hydroxide and carbonate resulting from partial neutralization, when plotted against the normality of the carbonate present, should fall on a straight line between k_o and k_n, in accordance with the principle introduced by Arrhenius, which may be stated: "In a mixture of two salts with a common ion, each salt has a degree of ionization equal to that which it would have when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture." In testing this principle Bray and Hunt[6] found in the case of sodium chloride and hydrochloric acid mixtures that the observed values of the specific conductance agreed very closely with the values calculated on the assumption that the degree of ionization, and hence the equivalent conductance, of each substance depended on the total salt concentration. In the present case the total salt concentration, $C_{KOH} + C_{1/2K_2CO_3}$, remains unchanged throughout the series of mixtures, from which it follows that the equivalent conductance

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[6] Bray and Hunt, THIS JOURNAL, **33,** 781 (1911).

of each substance does not depart from the value at 0.025 N, and the specific conductance of any mixture in the series should be

$$L = 253\ C_{KOH} + 126\ C_{1/2K_2CO_3}$$

or the conductivities in the present calibration units should be

$$k = (1.440\ N_{KOH} + 0.717 N_{K_2CO_3})/0.025$$

and since $N_{KOH} + N_{K_2CO_3} = 0.025$, this may be simplified to

$$k = 1.440 - 28.92\ N_{K_2CO_3}.$$

Experimental values for a and b were 0.0941 cm.^{3} and 1.43 cm.^{3}, respectively. For operation under a barometric pressure of 760 mm. of mercury, assuming aqueous vapor saturation, the number of moles m_{760} of dry gas per stroke would be

$$m_{760} = 1.602 \times 10^{-5}\ (760 - 23.5)b/298 = 5.67 \times 10^{-5} \text{ moles}$$

Hence the proportionality between the concentration $[CO_2]_{760}$ mole fraction of carbon dioxide in the gas and the normality of carbonate in the resulting solution would be

$$[CO_2]_{760} = aN_{K_2CO_3} \times 10^{-3}/2m_{760} = 0.830\ N_{K_2CO_3}.$$

By substituting in the expression for k above, there is obtained

$$[CO_2]_{760} = 0.0287\ (1.440 - k)$$

an equation by means of which the carbon dioxide concentration can be calculated directly from the milliammeter reading, when the barometric pressure is exactly normal.

The coefficient for the increase of m per mm. increase in barometric pressure is 0.001359, so that the value of $[CO_2]_P$ when the barometric pressure is P would be

$$[CO_2]_P = 0.0287(1.440 - k)/[1 + 0.001359(P - 760)]$$

It is obvious that the maximum concentration of carbon dioxide here capable of measurement with 0.025 N alkali is about 2%. The sensitivity depends mainly upon that of the electrical measurements. Thus in the present instance 0.002 milliampere is the equivalent of about 0.006% of carbon dioxide. In a given apparatus the range of concentrations measurable could be varied in direct proportionality to the titer of the alkali employed; the resulting sensitivity, assuming the adoption of a voltage suitable for the same range of currents, would be inversely proportional to the titer. To obtain greater sensitivity without resorting to an extremely weak absorbent, the apparatus itself could be modified by lengthening the tube CD. It may also be worthy of mention that in actual practice the range of an apparatus has been approximately doubled by the very simple expedient of causing each drop of liquid to halt about midway between C and D, continuing its descent only after the fall of the next drop, which results in changing the gas/liquid ratio from b/a to $(b-a)/2a$. This is accomplished by increasing the pressure in the tube Q just enough to balance the increased pressure above the goose-neck, for instance, by making the emergent gas bubble through about 1 cm. depth of oil.

Practical Uses

Two apparatus of this type have been found very advantageous at the Fixed Nitrogen Laboratory in the pursuit of several investigations relating to processes for the removal of carbon monoxide from hydrogen prior to the synthesis of ammonia. The one whose calibration has been described above is used for the estimation of up to 2% of carbon monoxide with a sensitivity of about one volume of carbon monoxide in ten thousand of the mixture; the other, which is connected to a recording instrument is capable of a sensitivity of about one part in thirty thousand in the range up to 0.75% CO. A third apparatus has been used tentatively for the estimation of ammonia in the presence of nitrogen and hydrogen, the absorbent being distilled water. It appears to be satisfactory for experimental work in which the concentration does not change rapidly, and with modification it should be possible to reduce the time lag so as to improve its ability to register fluctuations.

Though somewhat fragile, due to the necessity of glass in its construction, it could be shielded by inclosure in a cabinet; and since it requires no expert attention beyond the occasional renewal of the standard solution and the few other chemicals required for preliminary purification, there are indications that an apparatus of this type could easily be adapted for industrial process control.

Summary

1. An apparatus is described for the continuous automatic analysis of certain gases, utilizing the change in electrical conductivity of a solution that has been exposed to the gas in a device for controlling the volume ratio.

2. Two methods of calibrating the apparatus are given.

3. Among the gases capable of estimation by this means NH_3, HCl, SO_2, Cl_2, H_2S and CO_2 are mentioned.

4. An actual adaptation for the determination of CO in the presence of H_2 and hydrocarbons is described in detail.

5. Possibilities of extended use are indicated.

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