

[CONTRIBUTION FROM FIXED NITROGEN RESEARCH LABORATORY.<sup>1</sup>]

## A METHOD OF DETERMINING TRACES OF OXYGEN IN HYDROGEN.

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### Introduction.

In the synthesis of ammonia by the Haber Process a convenient and accurate method for estimating traces of oxygen in hydrogen-nitrogen mixtures is very desirable. None of the existing methods affords the degree of sensitivity and the rapidity of operation necessary to determine accurately the low concentrations to which this impurity must be limited.

One method which has been used for the estimation of oxygen consists in passing the gas over a contact mass which converts the oxygen into water; the water is then collected in an absorbent, usually phosphorus pentoxide, and weighed. In order to collect weighable quantities of water a very large volume of gas must be passed through the absorbent. For example, if the gas contains 0.001% of oxygen, 62 liters of the gas give only a milligram of water. Because of the difficulties involved in the complete absorption and the weighing of such small quantities of water, it is obvious that the method must be slow and inaccurate.

A colorimetric method has been developed which depends upon the conversion of colorless cuprous solutions into blue cupric solutions in the presence of oxygen. The intensity of this color change is made a measure of the oxygen content of the gas. This method has the advantage of being fairly rapid, but for very low concentrations of oxygen lacks the desired accuracy.

We undertook therefore the development of a rapid and accurate method of analysis for oxygen in hydrogen, where the concentration of oxygen might be as low as 0.001%. The success which had been met by Lamb and Larson<sup>2</sup> in the determination of low concentrations of carbon monoxide in air, suggested the possibility that this same principle at least could be applied to the estimation of oxygen in a large excess of hydrogen. In this method the combination of the trace of contained oxygen with the excess of hydrogen is catalyzed by platinum at 275–300°, and the temperature rise is measured by a thermocouple. The method is obviously not an absolute one; that is, the apparatus must be calibrated by the use of gas mixtures of known concentrations. This calibration of the apparatus proved, however, to be a very simple matter.

Since the temperature differences to be measured were very small, the needs of this work called for much closer regulation of the vapor bath

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> Lamb and Larson. *THIS JOURNAL*, **41**, 1908 (1919).

surrounding the platinum catalyst than had been found necessary in the work on the determination of carbon monoxide in air. That is, the accidental variations in the vapor bath might easily mask the temperature changes produced by the reaction on the platinum catalyst. The description of the apparatus and the discussion which follows will make evident the way in which the apparatus was designed so as to overcome these difficulties.

### Apparatus.

As shown in the accompanying diagram the apparatus consists essentially of a gas train, a platinum catalyst surrounded by an insulated vapor bath, a copper-constantan thermocouple, and a high sensitivity galvanometer.

A stream of purified hydrogen-nitrogen mixture (3:1) obtained by "cracking" ammonia was passed directly through the flowmeter C, or through the heated palladium-asbestos (350°) in B. Just ahead of the flowmeter was an adjustable regulator consisting of an outlet tube immersed in a movable column of liquid petrolatum. This outlet tube facilitated the close regulation of the gas flow. The meter was of the conventional capillary type, and found to be accurate within 0.5% for a flow of 500 cc. per minute.

At D there was joined to the train the outlet from an electrolytic cell E containing conc. potassium hydroxide solution. By suitably adjusting the resistance in F, the current from the storage battery G, as indicated by the milli-ammeter H, could be regulated to the value required for a given evolution of oxygen.

A 3-way cock J was provided so that the gas could be by-passed through the phosphorus pentoxide tube K before entering the catalyst

tube. L was a wax-sealed ground glass connection, the tubing beyond this point being of Pyrex glass.

The gas entered the preheating coil M, which was made from about 3 meters of 4 mm. tubing, the dimensions of the coil being about 30 × 3 cm. At N (see enlargement at right) the gas entered the outer tube O, of 10 mm. diameter, passing downward to its lower end, then up through the inner tube P, which contained the platinum gauze Q and the thermocouple junctions R and S. The "cold" junction R and its copper lead were insulated with a single piece of thin-walled capillary glass tubing shaped like the letter J. This insulation was found to be necessary in order to prevent premature catalysis on the surface of the copper wire at or near the "cold junction," an effect which might be sufficiently pronounced to generate an appreciable counter e. m. f. and even give a "negative" galvanometer deflection. The hot junction was imbedded near the top of the platinum catalyst. In order to diminish the Becquerel

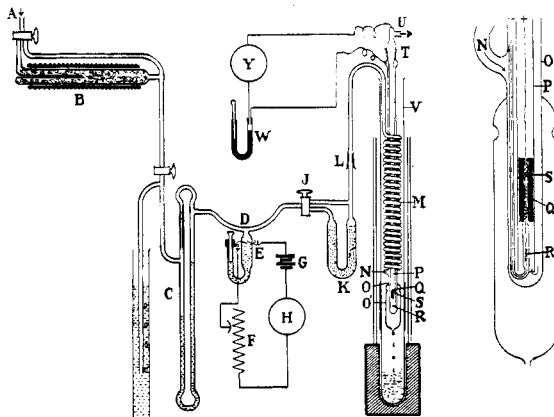


Fig. 1.

effect due to lack of homogeneity, the copper wire used was first subjected to careful annealing and subsequently handled in a manner to avoid excessive strains.

O' was a glass apron, sealed to O, and designed to safeguard the uniformity of temperature in that region, both by shedding the condensed liquid and by shielding the interior from other disturbances. Perforations near the top of this apron allowed free circulation of vapor, while the constricted aperture at the bottom prevented the entrance of superheated vapor.

The inner tube P was flared and ground to fit the mouth of the outer tube at T. This joint and the orifices admitting the copper wires were made air-tight with sealing wax. The gas emerged from the side arm U.

V was a Pyrex tube  $6 \times 70$  cm. employed as a vapor bath. It was insulated with an air jacket formed between it and an outer tube wrapped with asbestos paper. The 10cm. length immediately surrounding the "vital" zone was closely wrapped with sheet metal. The bath was heated by an electric furnace to a temperature just sufficient to keep the condensation zone a few cm. below the top of the tube V. Diphenylamine, boiling at  $305^\circ$ , was found a convenient substance for the bath, but it undergoes gradual alteration and had to be renewed occasionally. Diphenyl was also used and found to disintegrate less rapidly, but unfortunately its boiling point,  $255^\circ$  is very close to the minimum temperature at which platinum will completely catalyze the combustion of hydrogen. We found it safer to employ diphenylamine.

Y was a Leeds and Northrup high-sensitivity galvanometer giving a deflection of 11.0 mm. per microvolt when no external resistance was used. It was mounted on a rigid support and encased in a wooden box with a small glass window, the box serving to maintain a fairly uniform temperature at the contact posts. When readings were to be taken, the thermo-electric circuit was closed by raising the mercury level in the tube W, in which were inserted the ends of the two wires. The ordinary knife switch could not be used at this point because of the uncertain contact potentials which it introduced. No trouble was experienced with this mercury contact switch.

### Calibration.

The problem of obtaining a low-concentration gas of known oxygen content for use in calibration presented some unforeseen difficulties, but the method finally adopted proved very satisfactory. A constant flow of 500 cc. (N. T. P.) of purified hydrogen-nitrogen mixture was maintained through the apparatus, and was found to produce a slight negative deflection of the galvanometer. This deflection was reasonably constant and reproducible, and was employed as a blank correction for subsequent

TABLE I  
CALIBRATION AT FLOW OF 500 CC./MIN.

Date	Current through electrolytic cell Milli-amperes	Oxygen concentration %	Galvanometer (cm. scale)		
			Average reading	Average blank	Average deflection
May 6	2.12	0.00148	1.45	-2.30	3.75
	4.14	0.00288	5.60	-2.30	7.90
	6.27	0.00437	10.60	-2.30	12.90
	10.41	0.00725	20.70	-2.30	23.00
May 7	0.71	0.00049	-1.05	-2.25	1.20
	2.12	0.00148	1.55	-2.25	3.80
	3.14	0.00218	3.60	-2.25	5.85
May 10	10.41	0.00725	20.15	-2.85	23.00

readings. The calibration was then effected by passing through the electrolytic cell a succession of measured currents, allowing sufficient time at each setting for a uniform gas mixture to develop. Since each milli-ampere liberates  $82.9 \times 10^{-6}$  mg. of oxygen per second, an easy calculation gives the concentration resulting with a dilution of 500 cc. per minute. Readings of the galvanometer were then taken continuously for a period of 10 to 15 minutes, and were found to reach a very constant value within 5 minutes. These readings are given in Table I and are shown graphically in Fig. 2.

In the Table I, the average galvanometer reading represents the mean of ten or more observations at intervals of 30 seconds. Fluctuations from the average seldom exceeded 0.25 cm. Blanks on purified gas were taken frequently during the runs.

From the calibration curve it becomes a simple matter to determine the oxygen content of an oxygen-nitrogen-hydrogen mixture containing an unknown amount of oxygen. For example, on May 6, a gas which was known to contain 0.00582% oxygen was examined by this method. From the calibration curve the oxygen content was found to be 0.00585%;

likewise, on May 7, a gas containing 0.00077% oxygen showed 0.00079% by this method. From these results it would seem that the apparatus is satisfactory down to about 0.00003% of oxygen. In other words, in the estimation of a gas containing 0.001% oxygen the error would be about 3%.

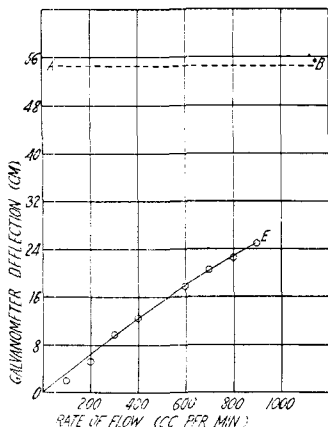


Fig. 3.

In this connection it was thought to be of interest to compare the observed galvanometer deflections with those that would be expected if the thermal system were 100% efficient, *i. e.*, if there were no heat losses to the surroundings of the combustion zone. Taking the average molar heat of the gas mixture at 305° as 7.034, and the heat liberated from  $5 \times 10^{-6}$  mols. of oxygen as 5.836 calories, the temperature rise of a 0.005% gas would be 0.83°. Assuming the thermo-electric power of the copper-constantan couple to be 60.0 microvolts per degree the e.m.f. would be 49.8 microvolts, and should produce a

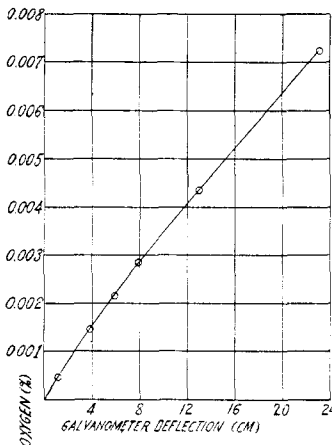


Fig. 2.

deflection of 54.8 cm. The experimental calibration curve gives 15.1 cm. as the actual deflection produced by a gas of this concentration at 500 cc. per minute, or about 28% of the calculated value.

It is evident therefore that the heat losses to the surroundings are quite considerable. The relation of rate of flow to these heat losses was determined by a series of experiments the results of which are recorded in Table II and shown graphically in Fig. 3.

TABLE II  
EFFECT OF RATE OF FLOW ON E. M. F. PRODUCED  
0.005% Oxygen

Rate of flow Cc./min.	Current through electrolytic cell Milli-amperes	Galvanometer (cm. scale)		
		Average reading	Average blank	Average deflection
100	1.44	-1.70	-3.80	2.10
200	2.87	1.90	-3.35	5.25
300	4.31	6.70	-3.20	9.90
400	5.75	9.70	-2.90	12.60
600	8.62	15.95	-1.70	17.65
700	10.06	19.10	-1.40	20.50
800	11.50	21.80	-0.70	22.50
900	12.93	24.60	-0.30	24.90

If there were no heat losses the galvanometer deflection would be a constant represented by the line A-B. It is evident from the manner in which the observed values are approaching this theoretical value A-B that a comparatively high flow must be reached before the variations in the rate would produce negligible effects upon the galvanometer deflections.

The thermal efficiency of the apparatus could no doubt be greatly improved by vacuum jacketing the catalyst, for example. If this were successful, the galvanometer readings obtained on a given gas would be less affected by variations in the rate of flow through the apparatus.

Or we might have increased the capacity of the preheating coils so that much higher rates of flow could have been employed. Probably with a flow of 2000 cc. per minute the effect of variations in the rate of flow would have been smaller. Since the exact regulation of the gas flow was a comparatively simple matter, we elected to calibrate the apparatus for a definite rate of flow. Even with the very great heat losses, it still had sufficient accuracy to make it reliable in determining the oxygen content of a nitrogen-hydrogen mixture.

Certain precautions were found necessary in the operation of this apparatus. First, the vapor bath was never heated until the apparatus had been thoroughly swept out with oxygen-free gas. While a large quantity of oxygen might not produce an explosion, still there is danger that the temperature of the catalyst would be raised to such an extent that its activity would be considerably diminished if not wholly destroyed. Sec-

ond, the galvanometer was always disconnected or short-circuited until the bath had reached the proper temperature.

It was found advisable, when extreme accuracy was desired, to make frequent observations of the "blank" correction that had to be applied to the galvanometer readings. Prolonged use of diphenylamine in the bath results in superheating of the lower or "cold" junction and a consequent negative galvanometer deflection of increasing magnitude. Other minor causes introduce slight variations. The method of making the "blank" observation consisted simply in by-passing the gas stream through the heated palladium-asbestos and allowing several minutes for the train to be swept with the purified gas.

Poisoning of the platinum catalyst may result from the presence of halogens or sulfur compounds. If the gas contains such impurities they must be completely removed before the gas is permitted to reach the catalyst. Extreme poisoning generally necessitates removing the platinum and reactivating it by purifying and replating.

The apparatus described in this article was designed to operate on a gas which did not contain oxygen in excess of 0.01%. Higher concentrations of oxygen would require the introduction of an external resistance in the galvanometer circuit or the use of a less sensitive instrument. However, if the apparatus be used to examine a gas whose oxygen content is much in excess of 0.1%, say, 1 or 2%, the activity of the platinum catalyst may be lowered considerably and much of the oxygen passed through without combining. By operating the whole catalyst at a higher temperature, say 400–450°, this difficulty would no doubt be obviated.

### Summary.

1. The necessity for an accurate and rapid method for analysis of oxygen in nitrogen-hydrogen mixtures has been explained.

2. A thermometric method which is both rapid and accurate has been described. In this method the gas mixture is passed through a platinized platinum catalyst where the temperature rise is measured by a thermo-element. Deflections of a galvanometer attached to this thermo-element are made the measure of the oxygen content of the gas mixture. Concentrations of oxygen as low as 0.001% may easily be determined, the error being about 3%.

3. A device for introducing a definite quantity of oxygen into the oxygen-free gas has been described. This facilitates calibration and checking of the apparatus. A specimen calibration curve has been included.

4. Attention has been called to the details in construction and the manipulation of the apparatus which will insure its successful operation.

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