CLXXXV.—*The Estimation of Carbon Monoxide.*

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SEVERAL methods for the estimation of carbon monoxide based on the reaction $\text{I}_2\text{O}_5 + 5\text{CO} = \text{I}_2 + 5\text{CO}_2$ have been described,* some involving the estimation of the iodine produced, others the carbon dioxide, the latter being usually absorbed by standard barium hydroxide, the excess of which is titrated with standard oxalic acid solution. The application of these methods to routine estimations of carbon monoxide is difficult owing to the cumbersome nature of the apparatus required, and the large volume of sample necessary. We have, therefore, devised an apparatus which is essentially a modification of the well known Haldane type of gas analysis

* For an excellent résumé of work on this object, see Weiskopf, *J. Chem. Metall. Min. Soc. S. Africa*, 1909, **9**, 258; compare also Goutal, *Ann. chim. anal.*, 1910, **15**, 1; Levy, *J. Soc. Chem. Ind.*, 1911, **30**, 1437.

apparatus, and in which iodine pentoxide is employed for the selective oxidation of carbon monoxide, so that the latter may be quickly and easily estimated volumetrically, yet, at the same time, so that an accuracy of 0.02 per cent. may be obtained, 20 c.c. of the sample being the volume required for an analysis.

The rate of oxidation of carbon monoxide by iodine pentoxide is determined largely by the temperature at which the reaction is carried out, and this has been one of the chief points of discussion between the various investigators of this subject. We have found that the reaction takes place slowly at 70—80°, but is rapid and complete at 90—100°, and have, therefore, finally adopted the latter range of temperature. The results of a number of analyses of mixtures of carbon monoxide and air (tables A and B) show that an accuracy of 0.02 per cent. may be readily obtained.

It is well known that unsaturated hydrocarbons affect the accuracy of estimations, and these must therefore be removed from the sample before passage over the iodine pentoxide. In the present investigation considerable attention has been given to the reaction of iodine pentoxide with hydrogen and saturated hydrocarbons at various temperatures. It seems to have been generally accepted that hydrogen is not acted on by iodine pentoxide. In the following pages, however, it is shown that hydrogen in the absence of carbon monoxide is attacked by iodine pentoxide at temperatures above 135°. When carbon monoxide is present, oxidation of the hydrogen takes place at lower temperatures as the percentages of these gases increase. When the concentration of hydrogen is above 20 per cent. it is impossible to oxidise the carbon monoxide without attacking the hydrogen to some small extent, even at temperatures below 100°. The nature of the action of iodine pentoxide in the presence of carbon monoxide is not quite clear, but it seems highly probable that, with mixtures of hydrogen and carbon monoxide containing comparatively large amounts of the latter (more than 8 or 9 per cent.), the hydrogen is attacked by the nascent iodine evolved in the reaction between the carbon monoxide and iodine pentoxide. The action of iodine pentoxide on hydrogen at higher temperatures (about 160°) appears, on the other hand, to be a simple case of oxidation of the hydrogen to water with liberation of iodine. In order to estimate carbon monoxide accurately by oxidation with iodine pentoxide, if the hydrogen exceeds 20 per cent., the sample must be suitably diluted with an indifferent gas. When, however, the hydrogen is below this limit an accuracy of 0.02 per cent. in the estimation of the carbon monoxide can readily be obtained on a sample of 20 c.c. by the method described in this paper.

EXPERIMENTAL.

Description of Apparatus and Analytical Results for Mixtures of Carbon Monoxide and Air.

The apparatus used is a modification of the well-known Haldane type of gas analysis apparatus, and is designed to measure the contraction which occurs when a mixture containing carbon monoxide is passed over heated iodine pentoxide and the products of the reaction are treated with potassium hydroxide. This contraction is equal in volume to the quantity of carbon monoxide present in the original sample. The usual absorption pipettes on the Haldane apparatus are replaced by three potassium hydroxide pipettes, a bromine pipette, and a U-tube containing about 2 grams of iodine pentoxide, arranged as shown in the figure.

A contains 25 per cent. potassium hydroxide solution. *C* and *E*, 45 per cent. potassium hydroxide solution, *B* bromine in an aqueous solution of potassium bromide, and *D* is a small U-tube so filled with powdered iodine pentoxide that the "dead space" in the tube is reduced to a minimum.

The potassium hydroxide and bromine pipettes are connected to suitable reservoirs. The pipette *C* is connected through a T-piece to the usual compensating device employed on the Haldane apparatus. After filling with pure iodine pentoxide, the U-tube is heated to 200° for three or four hours in a current of dry air, before being fitted to the apparatus. A broad wooden shield on either side protects the various pipettes from absorbing heat while the iodine pentoxide tube is being heated. The sample for analysis is taken into the burette and measured (1) with the usual precautions

adopted when using the Haldane apparatus, the U-tube of iodine pentoxide being immersed in a bath of cold water, the temperature of which is noted. The sample is then passed into the bromine pipette, *B*, where it is kept for four minutes, the burette tap and those leading to *A* and *C* being closed. By opening the necessary taps and lowering the reservoir attached to *C*, the sample is then transferred to the pipette *C*. The tap to *B* having been closed to the bromine pipette, the sample is passed several times backwards and forwards between *C* and *A* to remove all bromine vapour, and is then brought back into the burette and measured. The operation is repeated until a constant reading (2) is obtained. The difference between (1) and (2) gives the amount of carbon dioxide, hydrogen sulphide, sulphur dioxide, and unsaturated hydrocarbons. The latter are completely removed by two passages into the bromine pipette provided the amount does not exceed 5 per cent., the second passage only being necessary to "wash out" the "dead space" between the burette and the bromine pipette. The sample is next passed into the pipette *C* and the tap on this pipette opened to the U-tube, which is now heated to 90–100°, the beaker of cold water being replaced by one containing hot water and heated by means of a small Bunsen burner during the oxidation of the carbon monoxide. The sample is passed from *C* to *E* through the iodine pentoxide U-tube, *D*, twice backwards and forwards by raising or lowering the reservoir attached to *C*. By this means the carbon monoxide is oxidised to the dioxide, which, together with the iodine liberated, is absorbed by the alkali in *C* and *E*. The residual sample in the connexions between the burette, *A*, *B*, and *C*, is "washed out," and the gas sample again passed backwards and forwards twice over the hot iodine pentoxide. This has been found sufficient to remove completely all the carbon monoxide even when 15 per cent. is present in the original sample. (The complete removal of carbon monoxide has been demonstrated by constancy of volume after subjection to further passages over the hot iodine pentoxide, and also by the delicate "blood" test.) The beaker of hot water is then removed and replaced by the original beaker of cold water, and after a couple of minutes the potash level in *E* is brought to the graduation mark, the temperature of the water-bath being again noted. In cases where there is any small variation in temperature, a correction, readily determined by experiment, is applied. This correction should not exceed 0.002 c.c. per 1° change in temperature in a well-constructed iodine pentoxide tube. The sample is transferred to the burette and measured (3), the difference between (2) and (3) giving the amount of carbon monoxide present.

It will be noticed that the gas sample is confined over 45 per cent. potassium hydroxide solution during the oxidation, and is therefore not quite dry. Previous investigators have insisted that the sample must be free from moisture for complete oxidation of the carbon monoxide, but this is apparently unnecessary, although we have found it advisable to heat the iodine pentoxide to about 190° in a current of dry air after about twenty analyses. This is probably due to the fact that moisture has been present in the gas sample passed over the iodine pentoxide. For simplicity in manipulation the U-tube is connected to the apparatus by means of rubber junctions at *c* and *e*, no objection having been found to the adoption of this plan.

In the experiments described below, mixtures have been made from pure carbon monoxide, the purity of which has been controlled by combustion analysis in the Haldane apparatus.

TABLE A. *Mixtures of Carbon Monoxide and Air, Iodine Pentoxide (tube heated to 160 — 180°).*

Volume of carbon monoxide present in sample. c.c.	Carbon monoxide present. Per cent.	Carbon monoxide found. Per cent.	Error. Per cent.
0.004	0.02	0.02	± 0.00
0.015	0.08	0.10	$+0.02$
0.020	0.11	0.11	± 0.00
0.020	0.11	0.10	-0.01
0.039	0.22	0.22	± 0.00
0.070	0.39	0.38	-0.01
0.276	1.50	1.51	$+0.01$
0.568	3.06	3.09	$+0.03$

In the above determinations the pipette *E* contained mercury, and the gas was passed through the U-tube from the burette, the carbon dioxide produced being estimated by subsequent passage into the pipette *C*. The method described in the previous part of the paper was afterwards adopted owing to the contamination of the mercury in the burette and pipette, *E*, by the iodine liberated during oxidation.

TABLE B. *Mixtures of Carbon Monoxide and Air.*

Temperature.	Carbon monoxide present. Per cent.	Carbon monoxide found. Per cent.	Error. Per cent.
160—180°	3.43	3.41	-0.02
160—180	10.22	10.21	-0.01
130—140	24.13	24.14	$+0.01$
105—115	3.58	3.58	± 0.00
90—95	8.21	8.20	-0.01
90—95	16.12	16.13	$+0.01$

Influence of Hydrogen and Saturated Hydrocarbons on the Accuracy of the Method.

Mixtures of Hydrogen and Air.—The reaction between iodine pentoxide and hydrogen at various temperatures was investigated, and from the results given below it is clear that hydrogen is readily attacked by iodine pentoxide at temperatures above 135°.

TABLE C.

Temperature.	Hydrogen in sample. Per cent.	Carbon monoxide present. Per cent.	Contraction. Per cent.
100—105°	20	0.00	0.00
110—125	100	0.00	0.00
140—145	100	0.00	0.02
160—165	100	0.00	0.35
170—180	20	0.00	0.50
170—180	100	0.00	1.27

From the above table it appears that hydrogen alone is not attacked at temperatures below 130°. When, however, carbon monoxide is present, this temperature is considerably reduced. This reduction depends both on the concentration of the hydrogen and that of the carbon monoxide. Experiment shows that: (1) If the concentration of hydrogen exceeds 20 per cent., accurate estimation of the carbon monoxide is impossible. (Table D.) (2) If the concentration of hydrogen is less than 20 per cent. but greater than 6 per cent., and that of the carbon monoxide greater than 8 per cent., accurate estimation of the carbon monoxide is still impossible. (Table E.) (3) If the mixture contains less than 20 per cent. of hydrogen and less than 8 per cent. of carbon monoxide, an accuracy of 0.02 per cent. can be obtained (Table F), and (4) If the concentration of the hydrogen is below 1 per cent., up to 25 per cent. of carbon monoxide can be satisfactorily estimated. (Table G.)

It follows, therefore, that for accurate analysis of mixtures rich in hydrogen and carbon monoxide, the sample should be diluted with air to bring the concentration of the hydrogen below 20 per cent. and that of the carbon monoxide below 8 per cent.

TABLE D. *Mixtures of Hydrogen, Carbon Monoxide, and Air, in which the Hydrogen exceeds 20 per cent.*

Temperature.	Hydrogen. Per cent.	Carbon monoxide	Carbon monoxide	Error. Per cent.
		present. Per cent.	found. Per cent.	
90°	23.0	5.37	5.38	+ 0.01
120	23.0	5.37	5.43	+ 0.06
105—115	27.5	11.13	11.30	+ 0.17
100—115	28.0	4.70	4.73	+ 0.03
70—80	33.0	9.86	9.81	— 0.05*
100—115	35.0	4.08	4.25	+ 0.17
90—95	52.8	1.17	1.30	+ 0.13
90—95	68.2	0.72	0.79	+ 0.07
75—85	70.0	3.64	3.70	+ 0.06
100—110	80.0	2.82	3.07	+ 0.25
90—95	92.8	1.10	1.31	+ 0.21

* Incomplete oxidation at the low temperature employed.

TABLE E. *Mixtures containing between 6 per cent. and 20 per cent. of Hydrogen and more than 8 per cent. of Carbon Monoxide.*

Temperature.	Hydrogen. Per cent.	Carbon monoxide	Carbon monoxide	Error. Per cent.
		present. Per cent.	found. Per cent.	
90—95°	6.05	9.52	9.59	+ 0.07
90—95	6.05	12.41	12.57	+ 0.16
90—95	8.03	10.65	10.74	+ 0.09
90—95	18.57	9.73	9.90	+ 0.17
85—90	18.57	10.01	10.09	+ 0.08
85—90	18.72	9.57	9.70	+ 0.13
85—90	20.0	12.65	13.08	+ 0.43

TABLE F. *Mixtures containing less than 20 per cent. Hydrogen and less than 8 per cent. Carbon Monoxide.*

Temperature.	Hydrogen. Per cent.	Carbon monoxide	Carbon monoxide	Error. Per cent.
		present. Per cent.	found. Per cent.	
90—95°	6.38	5.47	5.47	± 0.00
90—95	8.30	8.44	8.44	± 0.00
95—105	14.0	7.39	7.38	— 0.01
95—105	14.0	7.45	7.43	— 0.02
90—95	18.80	7.87	7.88	+ 0.01
90—95	19.58	5.66	5.68	+ 0.02

TABLE G. *Mixtures containing less than 3 per cent. Hydrogen with large percentages of Carbon Monoxide.*

Temperature.	Hydrogen Per cent.	Carbon monoxide	Carbon monoxide	Error. Per cent.
		present. Per cent.	found. Per cent.	
90—95°	2.16	11.95	12.00	+ 0.05
90—95	2.00	14.27	14.36	+ 0.09
90—95	1.20	15.96	16.00	+ 0.04
90—95	1.04	24.85	24.95	+ 0.10

The action of mixtures of air with methane, containing a small percentage of its homologues ("natural fire-damp"), has been tested with samples containing approximately 10 per cent. and 80 per cent. of combustible gas. No oxidation is observed even when the sample is passed over iodine pentoxide heated at 160—180°. Artificial mixtures of these samples with small amounts of carbon monoxide were also analysed, the results being given below:

Temperature.	Fire damp. Per cent.	Carbon monoxide	Carbon monoxide	Error. Per cent.
		present. Per cent.	found. Per cent.	
160—180°	10.85	0.00	0.00	± 0.00
90—95	79.0	0.00	0.00	± 0.00
160—180	79.0	0.00	— 0.01	— 0.01
160—180	10.8	0.18	0.19	+ 0.01
160—180	10.7	1.12	1.15	+ 0.03
90—95	74.6	1.98	2.01	+ 0.03
90—95	70.6	2.60	2.59	— 0.01

As coal gas contains a large proportion of hydrogen, it is not possible to analyse an undiluted sample for carbon monoxide.

In the following analyses the samples were consequently diluted with air to about five times their volume in order to reduce the concentration of hydrogen to about 12 per cent. for the reasons already stated. If this be done, results which do not differ by more than 0.02 per cent. may be obtained for the carbon monoxide estimation, as shown by the following table:

	Sample A.			Sample B.		Sample C.	
	(1)	(2)	(3)	(1)	(2)	(1)	(2)
Coal gas, per cent.	23.17	23.17	23.17	21.04	21.04	21.98	21.98
CO ₂ , unsaturated compounds, etc., per cent.	1.18	—	1.18	0.96	0.95	1.10	1.08
CO per cent.	1.39	1.39	—	1.29	1.30	1.44	1.46

The necessary dilution can be made accurately in the gas burette of the apparatus. The residual gas after removal of the carbon monoxide by the analysis was tested for traces of carbon monoxide by the delicate "blood" test with negative results.

The authors therefore conclude that carbon monoxide can be estimated rapidly and with considerable accuracy by oxidation with iodine pentoxide by the method described, provided that the precautions detailed in this paper are observed.

A practical advantage of the method is that as only a few c.c. of the sample are needed for the analyses the same small sample which suffices for the determination of other constituents, such as oxygen, methane, or carbon dioxide, is sufficient also for determining carbon monoxide.