GASOMETRIC DETERMINATION OF FORMALDEHYDE.

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IN STUDYING the reaction which takes place when formaldehyde is brought in contact with potassium permanganate, it became necessary to know the exact amount of aldehyde expelled by the heat of combustion, together with the amount of carbon dioxide and formic acid, in order to determine the amount of aldehyde actually oxidized by the permanganate. To make these determinations as accurate as possible, various methods for the determination of formaldehyde were tried. In addition to the difficulties experienced in determining formaldehyde in the presence of formic acid and carbon dioxide, we were surprised to find that the common methods, which are regarded as accurate, would not check on all samples which we examined. Some of these methods gave comparatively concordant results with certain samples of aldehyde, while other methods gave results which varied as widely as 3 per cent. It therefore became necessary to find some quick method which would give as correct results as possible and at the same time be convenient as well as rapid in our calorimetric determination.

To obtain these results the common methods of determining formaldehyde were compared with each other. We began by trying the common ammonia method and its modified form by Smith,[1] together with the hexamethylene and the old alkaline method of heating the aldehyde with potassium hydroxide in pressure flasks. Finally, we studied the reaction mentioned by Blank and Finkenbeiner,[2] in which hydrogen peroxide is used together with an alkali. In examining the last-mentioned it was found that hydrogen in a pure state is liberated. It therefore occurred to us that perhaps this fact would afford a rapid, and at the same time an accurate, method of determining formaldehyde, gasometrically, in the presence of formic and carbonic acids.

When formaldehyde is brought in contact with a solution of sodium or potassium hydroxide a reaction takes place resulting in oxidation on the one hand, and reduction on the other, according to the well-known reaction:

$$2CH_2O + KOH = HCOOK + CH_3OH.$$

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[1] *Am. J. Pharm.*, **70**, 86.

[2] *Ber.*, **31**, 2979.

When, however, these two substances are brought together in the presence of hydrogen peroxide the reaction is changed, notwithstanding the fact that both oxidation and reduction take place. As above, potassium formate is formed, but in place of methyl alcohol, pure hydrogen is liberated, according to the following equation:

$$2CH_2O + 2KOH = 2HCOOK + 2H_2O + H_2.$$

One molecule of hydrogen is liberated for every two molecules of formaldehyde. A study of this reaction showed that the hydroxides of practically all of the light metals would liberate hydrogen in the presence of hydrogen peroxide, while the peroxides of the same metals would liberate hydrogen without the addition of hydrogen peroxide. The peroxides of the alkali metals produce an explosion when brought in contact with strong formaldehyde; if diluted with water, an energetic reaction takes place, liberating hydrogen, and when the reaction is too violent a small quantity of oxygen is liberated. In the same way the peroxides of the alkali earths act upon formaldehyde, but hydrogen is liberated very slowly without the addition of free hydrogen peroxide.

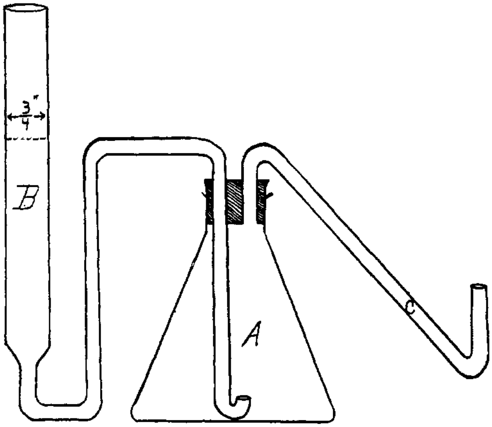

Fig. 1.

It first became necessary to test the purity of the hydrogen. For this purpose a special generator[1] was used. It consisted of an Erlenmeyer flask, A (Fig. 1), fitted with a double-bored cork.

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[1] This apparatus will be fully described later by one of us and Mr. Francis Frary under New Lecture Apparatus (see this JOURNAL, 27, 746). We have used this piece of apparatus very successfully in determining the hydrogen equivalent of zinc.

Through one hole is passed a funnel tube, *B*, the funnel part being a wide tube which prevents air bubbles from passing over into the generator when the reagent is added. A common delivery tube, *C*, is inserted in the other hole of the cork. The flask is filled with water free from air, and a few cubic centimeters each of formaldehyde and hydrogen peroxide are added. When the generator, including the delivery tube, is completely filled, a solution of potassium hydroxide is poured into the funnel. It passes over into the flask and there comes in contact with the aldehyde and the peroxide. Hydrogen is liberated and can readily be collected without containing even a trace of air. In our first determinations, distilled water, which had stood in the air for some time, was used both in the generator and in the gasometer. Several analyses gave 99.7 per cent. pure hydrogen. Later, water free from air was used, in which case the hydrogen proved to be chemically pure.

DETERMINATION.

Several different forms of apparatus were tried in determining the quantity of hydrogen liberated. The Scheibler-Finkner calcimeter, with a graduated tube of 300 cc. capacity, was finally selected as giving best results. The generator bottle used was one with a side tube, so that it could be shaken vigorously without danger of breaking. A pressure-bottle with a stop-cock was also tried in order to determine whether or not any aldehyde was carried over with the hydrogen.

For rapid work 1 cc. of aldehyde of known specific gravity was used, although good results were obtained with half that amount. The aldehyde is placed in the side tube of the generator, and 10 cc. of hydrogen peroxide and 20 cc. of normal potassium hydroxide are placed in the body of the generator. The generator is closed and the water in the measuring tube is brought to zero. After the temperature has become constant a small quantity of the mixture of peroxide and hydroxide is allowed to come in contact with the formaldehyde. Hydrogen is rapidly liberated with evolution of considerable heat. When the reaction is completed the apparatus is allowed to stand until the generator bottle has again reached the room temperature, when the volume of hydrogen is read off. With the corrected volume of gas it is a very simple matter to calculate the per cent. of formaldehyde. The exactness of the equation was proved by beginning with samples of known strength.

In making these comparisons it was found that when a large amount of hydrogen peroxide and strong potassium hydroxide were used the results obtained were a little higher than those obtained by the other methods. After experimenting with the strength of these reagents, we found that when 1 cc. of aldehyde was used with 10 cc. of hydrogen peroxide and 20 cc. of normal potassium hydroxide the results obtained checked very closely with other methods. The following table gives comparative results on the same samples:

	Method.			
Sample.	Hexamethylene.	Ammonia.	Alkali.	Gasometric.
D	37.76	37.89	38.16	38.26
"	37.70	37.90	38.09	38.16
"	37.58	38.04	38.16	38.16
"	37.66	37.81	38.28	38.60
"	33.26	33.35	33.82	34.00
F	33.12	33.62	33.77	34.20
"	33.62	33.52	33.91	33.96
"	33.09	33.32	33.88	34.00

In the above analyses the same amount of peroxide and the same amount of hydroxide were used, namely, 10 cc. peroxide and 20 cc. of normal potassium hydroxide with 25 cc. of distilled water.

THE USE OF SODIUM PEROXIDE INSTEAD OF HYDROGEN PEROXIDE.

It was found that sodium peroxide gave, with formaldehyde, the same peculiar reaction which hydrogen peroxide gives. When the aldehyde comes in contact with sodium peroxide, unless the aldehyde is considerably diluted, the reaction is exceptionally violent and now and then results in an explosion. If the peroxide is first cautiously dissolved in water so as to liberate little or no oxygen, and then brought in contact with formaldehyde, hydrogen is liberated according to the following equation:

$$2CH_2O + Na_2O_2 = 2HCOONa + H_2.$$

The best results were obtained by using 2 grams of peroxide dissolved in 50 cc. of water with 1 cc. of aldehyde.

The results obtained with sodium peroxide were a little higher than by the use of hydrogen peroxide, more than likely due to the liberation of oxygen on bringing sodium peroxide in contact with water. An average of five analyses with sodium peroxide was 36.29 per cent. of formaldehyde, while the average of the same number of analyses with hydrogen peroxide was 35.88 per cent.

We are sure however that physical conditions are largely the cause of the varying results.

In studying the results it occurred to us that perhaps a trace of alcohol or formic acid might account for the high results. Analyses were therefore made introducing both methyl alcohol and formic acid besides the aldehyde. In each case the results were slightly less, instead of more, as would be expected. The following analyses will give a comparison.

In all these analyses, 2 grams of sodium peroxide, 1 cc. of formaldehyde of known specific gravity with 50 cc. of water were taken. To this was added 1 cc. of methyl alcohol and 1 cc. of formic acid. Results of these analyses are given below:

Per cent. of aldehyde		
without alcohol or acid.	with alcohol.	with formic acid.
37.08	35.51	35.79
36.64	35.78	35.86
36.07	35.78	35.92
35.92	35.70	35.64

Similar results were obtained with hydrogen peroxide in the presence of methyl alcohol and formic acid, that is, lower results in the presence of methyl alcohol than in either of the other cases. A probable explanation is that part of the oxidizing reagent was used in converting the alcohol to formic acid. It was found that alcohol was slowly oxidized to formic acid. A large number of determinations were made with varying amounts of hydrogen peroxide. It was found that with an excess of peroxide the results checked well with those made in the absence of methyl alcohol. The following table will verify this statement:

Per cent. of aldehyde		
without alcohol or acid.	with alcohol.	with formic acid.
33.28	33.28	33.42
33.50	33.28	33.31

In these analyses proportions of 40 cc. of normal potassium hydroxide, 20 cc. of hydrogen peroxide and 1 cc. of formaldehyde of known specific gravity were taken.

THE ACTION OF BARIUM PEROXIDE ON FORMALDEHYDE.

Barium peroxide, in the presence of water, slowly acts upon formaldehyde, liberating hydrogen. In the cold the reaction is very slow and incomplete. When heated, a quantitative reaction seems to take place:

$$4CH_2O + Ba_2O_2 = 2(CHO_2)Ba + 2H_2.$$

The reaction takes place more readily in the presence of free hydrogen peroxide. The results, however, were lower than with sodium peroxide. An average of five analyses with sodium peroxide gave 34.88 per cent. of formaldehyde, while with barium peroxide and hydrogen peroxide an average of 32.9 per cent. was obtained.

THE ACTION OF MANGANESE AND LEAD PEROXIDES ON FORMALDEHYDE.

The dioxides of manganese and lead are practically inert with formaldehyde alone. If hydrogen peroxide is added, as in the case of barium peroxide, oxygen, instead of hydrogen, is liberated. The amount of oxygen seems to be entirely independent of the presence of formaldehyde. The reaction seems however to be more vigorous in the presence of formaldehyde. Further examination is being made.

That the reaction which takes place between formaldehyde and hydrogen peroxide in alkaline solution is quantitative, there can be no doubt. Several things must be taken into consideration, however, in order that accurate results may be obtained. Special attention must be given to temperature, as considerable heat is generated in the reaction. The quantities of the reagents also vary the results. Large amounts of hydrogen peroxide and potassium hydroxide give higher results than moderate amounts of the reagents. This may be remedied, however, by diluting the reagents.

With proper care in manipulation very concordant results may be obtained, and the presence of formic acid, methyl alcohol and other impurities do not interfere or change results.

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[CONTRIBUTION FROM THE ANALYTICAL LABORATORY OF THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION.]

THE DETERMINATION OF VANILLIN, COUMARIN AND ACETANILIDE IN VANILLA EXTRACT.

BY A. L. WINTON AND E. MONROE BAILEY.

THE Hess and Prescott method[1] for the determination of vanillin and coumarin soon after its appearance, was adopted as a

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[1] This Journal, 21, 256 (1899).