THE LIBERATION OF FORMALDEHYDE GAS FROM SOLUTION BY MEANS OF ITS ACTION ON POTASSIUM PERMANGANATE.

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Received July 28, 1906.

As indicated in this Journal (**27**, 714), when strong formaldehyde is brought in contact with powdered potassium permanganate, a violent reaction takes place liberating carbon dioxide, formic acid, a large amount of formaldehyde gas and producing a large amount of heat. Experiments extending over a number of years have been made with the object of determining the ratio between the amount of formaldehyde liberated and the amount of heat produced, or in other words, the amount of heat produced by the oxidation of a known amount of formaldehyde gas. The results of a large number of experiments showed that it is extremely difficult to obtain concordant results. It was found that the condition of the permanganate, whether in crystal form or whether coarsely or finely powdered, made a great difference in the reaction. The strength of the formaldehyde solution and the rate of flow upon the permanganate likewise made a great difference both in the percentage of formaldehyde liberated and in the amount of heat produced. In fact, so many variables entered into the reaction that the calorific determinations were laid aside for the time and the conditions under which the greatest amount of formaldehyde gas could be liberated by potassium permanganate studied.

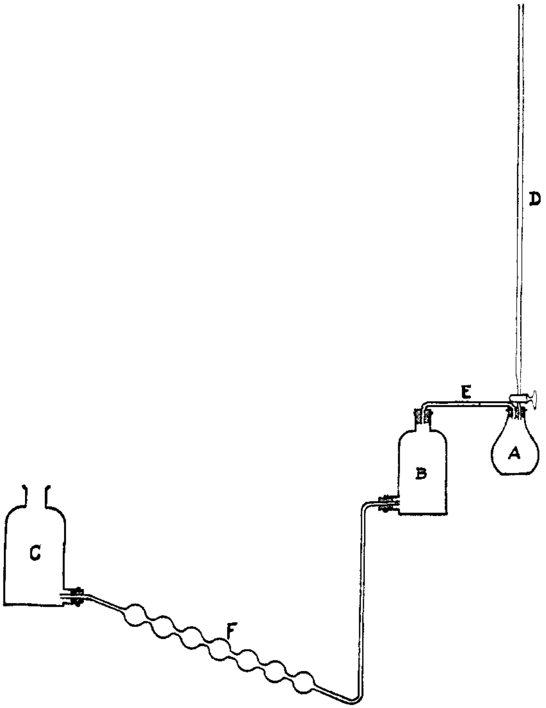
DETERMINATION OF FORMALDEHYDE.

Several obstacles were encountered in the determination of the amount of formaldehyde gas liberated by means of potassium permanganate. One of the first difficulties was in retaining the formaldehyde gas so that it could be accurately determined. The evolution of gas is usually so violent that the ordinary gas-bag stop-cock is not large enough to allow the gas to escape without producing an enormous pressure upon the generator; or in case of absorption of the gas it is extremely difficult to absorb all the gas either by water or by ammonia.

Another difficulty was experienced in bringing the formaldehyde solution in contact with the permanganate. If the aldehyde is allowed to drop on the permanganate from a burette, a crater of oxides of manganese is formed just where the aldehyde comes in contact with the permanganate, retaining the aldehyde so that after a short time the reaction almost stops. If, on the other hand, the formaldehyde is added all at once, the gas is liberated with explosive violence and at the same time the actual percentage of formaldehyde liberated is considerably less than when the formaldehyde solution is allowed to drop from a burette on the permanganate. In fact, several violent explosions were caused by adding strong formaldehyde solution to finely powdered permanganate. Frequently when 40 per cent. formaldehyde is slowly dropped on the powdered permanganate, a little flame is produced as each drop of formaldehyde strikes the powder. In this case the amount of formaldehyde is greatly diminished and the carbon dioxide greatly increased.

An attempt to overcome this violent reaction was made by diluting the formaldehyde with water. It was found, however, that while the addition of water modified the reaction, the quantity of formaldehyde gas was greatly diminished. Finally, the dilution of the permanganate by some inert substance was tried and found to give satisfactory results. The potassium permanganate was powdered and mixed with clean sand and the formaldehyde allowed to drop on this mixture. The sand prevented the formation of the crater of oxides of manganese. The formaldehyde percolated through the mixture and the reaction continued as long as the aldehyde was added and as long as there was unchanged permanganate left in the generator. As the gas is liberated from the solution by the heat of the reaction and as the specific heat of the sand is much less than that of water, more heat and hence more gas must necessarily be liberated by diluting the permanganate with sand than by diluting the formaldehyde solution with water. Notwithstanding the modifying effect of sand upon the above reaction, the change was still violent unless a large proportion of sand was used. It was found that a mixture of equal parts of sand and permanganate gave best results. With this proportion the reaction was violent but not to such an extent as to make the collection of the gas impossible.

Several forms of apparatus were tried. That indicated in Fig. 1 was adopted as giving satisfaction, whether the gas was collected in gas bags and measured or determined by absorption. A wide-mouth, short-neck flask *A* of about 200 cc. was fitted with



a double bored rubber stopper. Through one hole passed a burette for introducing a known quantity of formaldehyde. Through the other passed a delivery tube *E* of large diameter. This delivery tube was connected with an aspirator bottle *B* filled with water, one liter giving best results. The side neck of the aspirator bottle was connected with an absorption tube *F*. The absorption tube was so placed that the upper end was below the surface of the water in *B*, thus slightly diminishing the atmospheric pressure upon the gas. The other end of the absorption tube was connected with another aspirator bottle *C* which serves as a receiver in case the gas is not entirely absorbed as soon as it passes into *B*. If the reaction is very violent, forcing all of the water out of *B* into *C* by rapid liberation of gas, loss will be prevented by bubbling through the water in the absorption tube. At the end of the reaction the water is finally drawn back into *B*, but is prevented from being drawn over into *A* by the air which filled the generator at the beginning of the experiment. Usually, the absorption-tube is unnecessary except as a connecting tube between *B* and *C*. When all the gaseous formaldehyde has been absorbed by the water, it is thoroughly mixed, measured and the formaldehyde determined. During the reaction the temperature in the generator is practically constant at the boiling-point of water.

In the following table of analyses the solution used was 37.8 per cent. formaldehyde and the permanganate used was mixed with an equal amount of sand. The quantity of water used in absorbing the gas was varied, but 500 to 1000 cc. seemed to give the best results when 50 cc. of the formaldehyde solution were used. With very large quantities of water the solution became so dilute as to make an exact determination of formaldehyde somewhat difficult

	$KMnO_4$ + Sand. Grams.	Formaldehyde solution. cc.	Volume of water used in absorption. cc.	CH_2O liberated. Per cent.
1	100	50	1000	69.12
2	100	50	1000	71.42
3	100	50	1000	69.12
4	100	50	1000	67.96
5	150	50	1000	65.92
6	150	50	1000	63.53
7	200	50	1000	71.77
8	200	50	1000	70.00
9	200	50	1000	70.00
10	200	50	1000	65.00
11	200	50	1000	65.00
12	200	50	500	64.53
13	200	50	500	64.53
14	200	50	500	64.53
15	200	50	500	67.43
16	200	50	500	67.53
17	200	50	500	64.53
18	200	50	500	62.21
19	200	50	500	64.53

A large number of determinations were made, varying the time of reaction or the rate of flow of formaldehyde solution on the permanganate. The following table gives the average percentage of gas liberated:

Number of analyses.	Time of reaction. Minutes.	CH_2O. Per cent.
3	80	65.96
3	60	68.06
6	45	73.11
3	30	74.56
2	15	73.56
9	10	70.48

In these determinations 200 grams of the mixture of sand and permanganate and 50 cc. of 38 per cent. formaldehyde were used. During the process a considerable quantity of water distilled over. The greater part of the water came from the formaldehyde solution; a small quantity was formed by the oxidation of the formaldehyde. Measurements showed that about 45 cc. distilled.

The above averages indicate that with the quantities of permanganate and formaldehyde used in these experiments, the best results were obtained by allowing thirty minutes to complete the reaction. When more than that is taken, the amount of formaldehyde liberated seems to decrease and the amount of carbon dioxide to increase. With less than thirty minutes to complete the reaction, the amount of formaldehyde decreases and the amount of carbon dioxide seems also to decrease. Determinations of both carbon dioxide and formic acid are now being made.

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NOTES.

A Modification of the Hanging Drop Fluoride Test.—The necessary apparatus consists of a test-tube of small bore and about 2 inches long (a litmus-paper bottle serves admirably), fitted with a rubber stopper. The latter carries a small bit of glass tubing, closed at one end and inserted in the bottom of the stopper so that the open end shall extend about 3 mm. into the tube.

The precipitate of calcium carbonate and calcium fluoride, ignited until nearly free from carbonate, is well mixed with about 0.1 gram of precipitated silica and introduced into the dry tube. The bit of glass tubing is nearly filled with a couple of drops of water, the bottom of the stopper wiped thoroughly dry, and the latter inserted into the tube immediately following the addition of 1 to 2 cc. strong sulphuric acid. Place the tube in a beaker of water at the boiling-point and maintain at this temperature for fifteen to thirty minutes. If the substance under examination contained any appreciable quantity of fluoride its presence will be promptly indicated by the formation of a heavy gelatinous ring that not infrequently completely fills the end of the tube in the stopper.

In the writer's estimation, this procedure is far preferable to the troublesome and occasionally somewhat uncertain etching