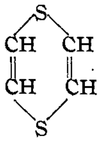
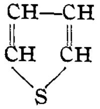
tion of a deep red color, as in the case of sulfuric acid, but this gradually disappears and an orange colored substance finally deposits. This is probably a nitro-derivative and is practically insoluble in alcohol, water and glacial acetic acid, but crystallizes from benzene in yellow needles. The dithiene also reacts immediately with bromine. If some of the sulfur compound is dissolved in glacial acetic acid and a drop of bromine is then added, the solution assumes at once a beautiful, dark blue color. This slowly disappears, however, and a dark colored product finally deposits from the acid solution. These interesting reactions will be investigated later.

Addenda.

1,4-Dithiene VI, corresponding to thiophene XXI, and the mother



VI.



XXI.

substance of 2,5-diphenyl- and 2,5-ditolyl-1,4-dithienes, is not described in Beilstein's Handbuch nor in Richter's Lexikon der Kohlenstoff Verbindungen. A careful search of the literature, however, has revealed the fact that this interesting compound was synthesized in 1889 by Louis E. Levi.[1] He prepared it by heating phosphorus trisulfide with thiodiglycollic acid, $S(CH_2COOH)_2$ and described it as an oil, which boiled at 175–180°. The yield, however, was very small. Levi assigned the name *biophene* to this substance. He also applied Freidel and Craft's reaction successfully and obtained the corresponding acetyl- and benzoyl-derivatives. Both of these compounds were oils. The acetylbiophene was identified in the form of its phenylhydrazone, which melted at 128°. Benzoylbiophene boiled at 241° and underwent nitration giving a crystallin mononitro-derivative melting at 112°. Dr. Levi writes me that this work on *biophene* originated in the laboratory of Professor Dr. Victor Meyer, Göttingen, while he was employed as Professor Meyer's private assistant.

NEW HAVEN, CONN.

AN IMPROVED APPARATUS FOR THE DETERMINATION OF CARBOXYL GROUPS IN ORGANIC ACIDS.[2]

BY W. H. HUNTER AND J. D. EDWARDS.

Received January 31, 1913.

Fritz Fuchs[3] has described a very simple and neat method for the determination of carboxyl groups, which depends on the fact that even

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[1] *Technol. Quarterly*, 3, No. 2; *Chem. News*, 62, 216; *Centrabl.*, 2, 949 (1890).

[2] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[3] *Monatsh.*, 9, 1132, 1143 (1888); 11, 363 (1890).

weak organic acids will immediately disengage hydrogen sulfide from solutions of potassium hydrosulfide, saturated with hydrogen sulfide.

The equation involved is:

$$RCOOH + KSH + xH_2S = RCOOK + xH_2S + H_2S,$$

one molecule of hydrogen sulfide being evolved for each carboxyl group.

The method possesses the great advantage over the titration method that, since the reagent is a solution acid with hydrogen sulfide, most lactones, and alcohols or phenol hydroxyl have no effect, with the following exceptions noted by Fuchs:

1. Halogenized phenols with two hydroxyls react with one hydroxyl.
2. Phenols with a single nitro group, if para, will react.
3. A few phenols with carbonyl present, as methyl phloroglucinol, may react.
4. An extremely weak acid, such as stearic acid, or one whose potassium salt is insoluble in the hydrosulfide solution, will not react.

As the method was first suggested, the hydrogen sulfide evolved was to be determined iodimetrically after absorption in alkali, or the hydrogen evolved by its action on mercury was to be collected. Later the principle of the Victor Meyer vapor density apparatus was used, so that the evolved hydrogen sulfide expelled from an air chamber an equal volume of air, which was then measured in a eudiometer. The present paper is concerned with an improved, accurate apparatus for carrying out the determination in the last manner.

The old apparatus, as described by Hans Meyer,[1] consists of a long-necked flask with thick walls, an air chamber, with delivery tube, and a device for dropping in the sample. The 10% potassium hydroxide used is freed from carbonate by a slight excess of barium hydroxide solution and filtered, then saturated with hydrogen sulfide. Some of this gas is left in the reaction flask at the beginning of the experiment, and then the stopper bearing the sample in one opening, and connected with the air chamber filled with dry air, by a tube in the other opening, is fitted gas-tight to the flask. The apparatus is then allowed to stand till it cools after handling, the delivery tube is brought under the receiver, a eudiometer, and the sample is dropped in by pushing the glass rod through to mark 2. The solution may be used for a second and third determination, by removing the air chamber and refilling it with dry air.

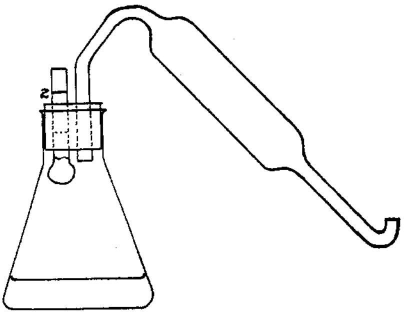

Fig. 1.—Apparatus of Fuchs.

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[1] Analyse and Konstitutions-ermittelung org. Verbindungen, 2 Auflage, p. 577.

Carried out in this manner, the determination is subject to a large number of errors, some of which may be easily avoided.

The most important source of error is the saturation of the solution with hydrogen sulfide. It is extremely difficult to reach a definit end point when the gas is simply allowed to bubble through the solution. In the formation of the strongly hydrolyzed hydrosulfide, the amount of gas taken up by the solution, and dissolved as such, has, of course, a direct effect on the amount of hydrosulfide formed. Now the amount of this dissolved gas obviously depends on the partial pressure of hydrogen sulfide in the gas phase above. For these reasons, special precautions must be taken to eliminate chance in the reaching of a definit equilibrium point in saturating the solution with hydrogen sulfide. Also, if the solution is not saturated, the hydrogen sulfide set free in the determination is certain to be partly taken up, and if the solution should chance to be supersaturated by earlier saturation under pressure, the reaching of equilibrium is slow on simple release of pressure, and the evolution of gas by the sample would certainly carry out with it much excess of gas.

Second, there is no way of telling when the large apparatus has reached constant temperature, and a change in temperature in the large volume of gas in the apparatus produces a change which may make a large error in the relatively small amount of gas evolved.

Third, in the large volume of the apparatus, the back pressure of water in the delivery tube leading to the eudiometer makes a noticeable difference in the volume of gas, as is always found on delivering gas into a eudiometer from a bent delivery tube.

Fourth, convection currents may carry hydrogen sulfide up to the top of the air chamber, if this is not rather long, in which case some will be carried over into the water and lost by solution.

Fifth, the vapor pressure of water over 10% hydrosulfide solutions is unknown. The dry air expelled is collected over water, and calculated back to dry hydrogen sulfide, whereas the gas is really saturated with water vapor at this unknown pressure. This causes a positive error of considerable magnitude. For instance, if the vapor pressure were as great as that of pure water, at 20° and 760 mm. 2.29% of the gas passing into the air chamber would be water vapor, leading to a positive error of 2.34% in the determination.

The large error just mentioned is opposed by the sixth, a negative error. It is an important, yet unavoidable one, due to the partition of the potassium cation between the hydrosulfide anion and the anion of the acid introduced. With a solution saturated with hydrogen sulfide, if more undissociated hydrogen sulfide is formed, it cannot remain dissolved, but must escape, leaving always a definit concentration of hydrogen ion present. This allows us to neglect the hydrolysis of the hydrosulfide, but when a new acid is introduced, partition of the base must occur. according to the law of concentration effect.

Henderson[1] has already discussed very completely the equilibria between weak acids and bases in solution. It is therefore unnecessary to say more than that if no other errors were present, it would be possible to calculate the per cent. of hydrogen sulfide which should be evolved, or even to read it from the valuable table given by Henderson, provided the final concentration of hydrogen ion were known. Since it is not known, it may be well to indicate the order of magnitude of the error, although in the 2 *N* hydrosulfide solution, the ratios involved are probably very different from those used in the following calculation: In *N*/10 solution, the percentage degree of dissociation of hydrogen sulfide is given as 0.075, by Walker and Cormack,[2] and for acetic acid Kohlrausch and Holborn[3] give 1.30. Therefore, if acetic acid and hydrogen sulfide were competing for the potassium hydroxide in *N*/10 solution, the base would be shared in the ratio 1.30 : 0.075, and the acetic acid would get but 94.54% of the base.

Other errors of less importance may well occur, due to adsorption of hydrogen sulfide, to difference in solubility of hydrogen sulfide in the salt solution formed, to the solubility of barium carbonate in strong potash solutions, and to the volume occupied by the sample.

The first four errors mentioned are readily avoided by the new apparatus, leaving only the partition effect and the error due to water vapor uncorrected. The apparatus used by the authors consists of a wide-mouthed reaction chamber *D* about 50 mm.

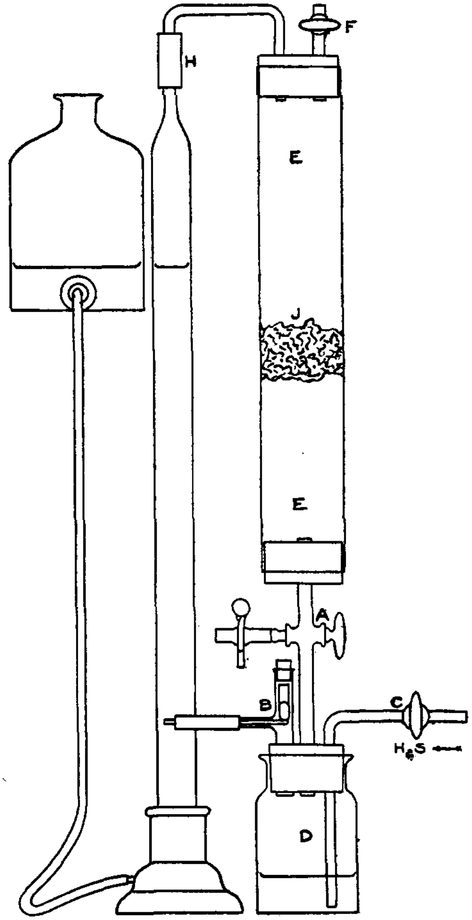

Fig. 2.

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[1] This Journal, 30, 955 (1908).
[2] *J. Chem. Soc.*, 77, 20 (1900).
[3] Leitvermögen der Elektrolyte.

internal diameter, and 80 mm. from bottom to neck. It is fitted with a rubber stopper bearing three holes. In one hole is placed a sample holder *B* of the type used on the Victor-Meyer vapor density apparatus. In another there is a delivery tube, *C*, for hydrogen sulfide, fitted with a glass stopcock. In the third is inserted a three-way cock, *A*, of such a type that either the reaction chamber or the air chamber, *E*, on the other end may be connected with the atmosphere, while the other compartment is closed, or a direct connection may be made between *D* and *E*. On the outlet to the air is a narrow rubber tube, which may be closed by a pinchcock. The air chamber, *E*, is about 37 mm. in internal diameter, and the open space between the heavy rubber stoppers is about 360 mm. in length. Midway in this space there is placed a loose plug, *J*, of glass wool. The rubber stopper in the top of *E* has two holes, one carrying a glass stopcock, *F*, connecting to the outside air, the other bearing a delivery tube without stopcock. All glass to rubber joints are made up with a layer of rubber cement, and all the glass tubes are set in with benzene into the rubber stoppers. The trigger of the sample-holder is also set in the piece of heavy rubber tubing with benzene. As a result, the apparatus is perfectly gas-tight when properly set up, the only weak point being the rubber connection, *H*, between the gas buret and the delivery tube, which becomes porous with repeated stretchings.

Procedure.

Test for Tightness of Apparatus.—The apparatus is set up just as for use, except that no sample is present, and the solution is not placed in the reaction chamber. The gas buret is attached, all outlets are closed, and the leveling bulb is dropped, and the reading taken on the buret. The level in a tight apparatus becomes constant almost immediately after the first cooling is compensated for. The effect of a leak in the apparatus is readily distinguished from the effect of a change in temperature. The glass over the gas spaces of course must not be touched by the hands at any time. If the apparatus is tight, the buret is detached, and gentle suction is applied at the three-way tap, drawing through the air chamber for at least five minutes, air dried by passing through a calcium chloride tube and a small phosphorus pentoxide tube. Then 25 cc. of carbonate free potash solution, about 1.5–2N, are introduced into the reaction chamber by a pipet, through the sample holder—if possible without wetting the tube, as the sample may stick in a wet tube.

Saturation with Hydrogen Sulfide. — The following definit conditions have been decided on as the result of experiment: The apparatus is set up in a place free from air currents, with the drying tube still attached. The three-way cock is turned to connect the reaction chamber with the air, and hydrogen sulfide is allowed to run in until all the air is expelled, to avoid decrease in the partial pressure of the gas over the solution.

The expulsion of air may be proven, if desired, by the use of a Schiff nitrometer with caustic potash, as in a nitrogen determination. A pinchcock is now fastened on the outlet tube, as the neutral point on this type of cock is not safe, the sample holder is opened to let out air, the sample is introduced, and the stopper replaced. When the gas ceases to bubble into the solution, the reaction chamber is held by the upper edge and shaken well for five minutes. The pinchcock is now removed from the outlet tube and the solution shaken three minutes with the gas flowing through. The stream is then slowed down, but allowed to continue till just before the sample is dropped, to sweep out any possible excess of gas. As the solution is appreciably warmed by the reaction when the fresh alkali is first neutralized by hydrogen sulfide, it must be allowed to stand for half an hour, before proceeding with the tests. This is obviously only necessary before the first determination.

Test for Constant Temperature in the Air Chamber.—The gas buret, leveled at about 99 cc., is now connected with the air chamber and leveled again. The heat of the body is sufficient to cause a change here, if care is not taken to avoid getting unnecessarily close to the apparatus. In two minutes, the level of the water in the buret should not change more than 0.1 cc. This is best observed by opening the stopcock, *F*, at the top of the air chamber at the end of the two minutes, when any change in level is at once visible.

Test for Constant Temperature of the Whole Apparatus, and Saturation with Hydrogen Sulfide.—When the air chamber is at constant temperature, the hydrogen sulfide is cut off, and connection is made between the reaction chamber and the buret. The whole apparatus is thus connected, and all outlets closed. The gas buret is again leveled, and the reaction chamber is held by the top and shaken two minutes. If no change in level greater than 0.1 cc. is observed in two minutes, the apparatus is ready. If change occurs, the measured shaking is repeated. Very rarely at this point two or three successive tests have shown a change in level of 0.2 cc. in two minutes. In such cases no great error is introduced if the determination is at once carried out, and 0.2 cc. correction applied. This was done in the last two analyses on tartaric acid. It is probable that the proper correction to apply in such a case would be a little greater than 0.2 cc., but the great uncertainty of such a correction makes it seem best to use the smaller correction. It would seem very unwise to apply such a correction, if the change in level were greater than 0.2 cc.

The Determination.—After a satisfactory final test, the buret reading is taken, and the sample dropped into the reaction chamber. The gas is at once evolved, aided by shaking if necessary. During the evolution, the level in the gas buret must be followed closely by the leveling bulb.

When the evolution ceases, the reading is taken rapidly, and then the reaction chamber is agitated vigorously for three minutes. The final reading is then taken, and will generally show an increase in volume, though this does not always occur, practically all the gas being evolved at once by some acids. The temperature and barometer are then observed.

To repeat the determination, it is only necessary to fill the air chamber again with dry air, and follow the procedure as before from the start of the five-minute shaking with hydrogen sulfide under pressure. A fresh solution should be used after the evolution of 100–125 cc. of the gas. The results of succeeding experiments should check within one per cent. of error very easily, and under favorable conditions, with little practice, much closer work can be done. A sample weighing 0.1800 gram with the barometer at 760 mm., and $t = 22.5$, reads directly in per cent. of COOH on the gas buret.

The only part of the apparatus which need ever be opened is the reaction chamber *D*, when the used solution and tubes are taken out.

The results may be calculated either by the formula given by Hans Meyer, giving the weight of replaceable hydrogen:

$$\text{Wt.H} = \frac{\text{V}(b - w)0.00000005895}{1 + 0.00367t}$$

or by the following, giving the weight of carboxyl:

$$\text{Wt.COOH} = \frac{\text{V}(b - w)0.000002632}{1 + 0.00367t}$$

In these formulas,

V = volume of gas evolved.

b = barometric pressure.

w = vapor pressure of water at $t°$

The two constants are calculated from the weight of 1 cc. of hydrogen and include the necessary division by two for the dibasic hydrogen sulfide, and by 760 for the reduction to normal pressure.

One source of error peculiar to the new method is that if the hydrogen sulfide is impure, as for instance from ferrous sulfide containing iron, the partial pressure will be less than that of pure gas, and the solution will contain less until the evolution of fresh pure sulfide in the determination, when a layer of pure gas covering the liquid may easily cause a further saturation, thus causing a retention of some hydrogen sulfide. Though this error cannot be large, if the gas used is at all pure, it is very easily eliminated entirely by using hydrogen sulfide evolved by the action of dilute sulfuric acid on concentrated sodium hydrosulfide solution. The sodium hydroxide solution is well saturated by hydrogen sulfide from an ordinary generator, and then acid is allowed to drop slowly into a funnel inside the generator for pure gas, the bell of the funnel being above the liquid, and the end of its tube turned up at about an inch from the end. By this arrangement, after the funnel tube has been cleared of hydrosulfide solution by the descending acid, the evolution of gas becomes regular, and the solution is well stirred.

The effect of impure gas was observed in that it was impossible to check closely work done on different days, until the pure gas was used.

The results obtained by the authors with the new apparatus are given in the following table, together with a set obtained by a student with the new apparatus, by another student with the old apparatus, and by Hans Meyer and Krczmar[1] on cantharic acid using the old apparatus:

TABLE OF RESULTS.

New Apparatus.

	Per cent. COOH.	Aver. found.	$\frac{\text{Av.} \times 100}{\text{Calc.}}$	$K \times 10^4$.	No. of det.	Extreme diff.
Crotonic	52.33	51.11	97.67	0.215[2]	3	0.27
Anisic	29.60	28.89	97.60	0.32[3]	3	0.21
Benzoic	36.89	36.11	97.59	0.686[2]	3	0.10
Salicylic	32.61	31.92	97.88	10.6[2]	3	0.24
Tartaric	60.00	60.47	100.79	9.7[3]	4	0.39
Maleic	75.85	76.34	100.64	154.0[2]	3	0.42
	Student's Series. First omitted.					
Anisic	29.60	28.63	96.74		3	0.75
	Old Apparatus—Student's Series. First omitted.					
Salicylic	32.61	21.77	66.75		3	2.24
Cantharic	34.18	30.77	88.85		3	3.74

The foregoing table shows immediately the efficiency of the apparatus, in comparison with the old one. The precision of the results obtained shows clearly that all the important errors have been eliminated, save the two unavoidable ones.

The action of these two is very apparent. It will be noticed that the column $\frac{\text{Av.} \times 100}{\text{calc.}}$ shows that the monobasic acids all give results consistently about 2.4% low, increasing a little with the increase in strength to salicylic acid. The two dibasic acids, however, give results about 0.7% high. This is just what is to be expected from the combined effect of the errors mentioned. The monobasic acids are not a great deal stronger than hydrogen sulfide, though the salicylic acid is much stronger than the others. Therefore the partition effect is rather large, approaching the effect calculated for acetic acid in $N/10$ solution, the affinity constant for acetic acid, $K \times 10^4 = 0.18$, being of the order of those of the first three acids.

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[1] H. Meyer and Krezmar, *Monatsh.*, **19**, 715 (1898).

[2] Ostwald, *Z. physik. Chem.*, **3**, 246, et seq.

[3] White and Jones, *Amer. Chem. J.*, **44**, 197 (1910).

Now in the presence of a much weaker acid, and a large amount of potassium ion, the dibasic acids may conveniently be viewed as acids one-half of which is very strong, or as acids in which one carboxyl is practically completely transformed into potassium salt, while the other then dissociates and shares the base with the hydrogen sulfide. One-half of the acid is then practically free from the negative error of partition, and the positive error of the water vapor causes the whole yield to cross the one hundred per cent. mark. That this is probably the true explanation is shown by the fact that the tartaric acid is very close in strength to the salicylic acid, but much weaker than the maleic acid, yet the yield of gas from the tartaric acid agrees with the maleic rather than with the salicylic yield, though agreement with the latter would be expected if only relative strength of acids were concerned.

It may then be expected that monobasic organic acids of ordinary strength will give results from two to two and one-half per cent. low, while dibasic acids will give results about seven-tenths per cent. high.

It is obvious that application of this apparatus may be made to other determinations.

Experimental Part.

Experiments on Saturation with Hydrogen Sulfide.—All the experiments to be described were made with hydrogen sulfide produced by the action of sulfuric acid on a concentrated sodium hydrosulfide solution.

The reaction chamber being closed for saturation under pressure, it was found that after no more hydrogen sulfide would bubble into the quiet apparatus, more was readily taken up on shaking the reaction chamber rather vigorously. On shaking for five minutes, it was found that it took a full minute more for one more bubble of gas to be delivered, and this was taken as showing that on shaking five minutes the solution had become sufficiently saturated under pressure for our purpose.

At the end of a determination it was found that by vigorously shaking the reaction chamber, more gas could be freed from the solution. Practically all is given off in two minutes, usually only 0.1–0.2 cc. being obtained in the third minute. Three minutes was therefore chosen as the time of shaking for expelling any excess gas during the saturation as well as for obtaining the last amount of gas in a determination.

On Constancy of Temperature.—The apparatus connected with the gas buret, with all outlets closed, becomes a large air thermometer. In a sheltered part of the room, with reasonably constant temperature, no difficulty is experienced in having the temperature so constant that the level will not change more than 0.1 cc. in two minutes, and in many determinations no change has been observed in that time.

Hydrolysis of the Hydrosulfide.—In the hydrosulfide solution ready for analysis, phenolphthalein gives no pink color. If a drop or two is allowed to stand in the air a few minutes, a pink color will be given by phenolphthalein, after the loss of hydrogen sulfide.

Details of Determinations.—The procedure was followed exactly as given. The acids were all pure samples of tested melting point.

Stearic acid was found not to set free any hydrogen sulfide from the solution:

Crotonic acid. Calc. COOH = 52.33%.
Found, 50.93, 51.20, 51.20. Av. 51.11%. Av. × 100/calc. = 97.67.
Anisic acid. Calc. COOH = 29.60%.
Found, 28.99, 28.78, 28.90. Av. = 28.89%. Av. × 100/calc. = 97.60.
Benzoic acid. Calc. COOH = 36.89%.
Found, 35.95, 36.01, 36.05. Av. = 36.00%. Av. × 100/ calc. = 97.59.
Salicylic acid. Calc. COOH = 32.61%.
Found, 31.85, 32.07, 31.83. Av. = 31.92. Av. × 100/calc. = 97.88.
Tartaric acid. Calc. COOH = 60.00%.
Found, 60.67, 60.28, 60.53, 60.65. Av. = 60.47. Av. × 100/calc. = 100.79.
Maleic acid. Calc. COOH = 75.85%.
Found, 76.14, 76.56, 76.33. Av. = 76.34. Av. × 100/calc. = 100.6.

Student's Series.—These were carried out by a student absolutely unfamiliar with the method. The first four determinations are given, and the first is excluded from the average, as a practice determination:

Anisic acid. Calc. COOH = 29.60%.
Found, 27.54, 28.26, 29.01, 28.62. Av. = 28.62. Av. × 100/calc. = 97.74.

Old Apparatus.

For comparison may be taken two sets of results obtained with the old apparatus:

1. By a student unacquainted with either apparatus:
Salicylic acid. Calc. COOH = 32.61%.
Found, 21.74, 20.66, 22.90. Av. = 21.77. Av. × 100/calc. = 66.76.
2. *Cantharic acid.*[1] Calc. COOH = 34.18%.
Found, 30.26, 32.3, 28.56. Av. = 30.37. Av. × 100/calc. = 88.85.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.

[FROM THE LABORATORIES OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS AND JEFFERSON MEDICAL COLLEGE.]

STUDIES ON WATER DRINKING. XIV. THE DIGESTIVE EFFICIENCY OF SALIVA AS INCREASED BY DILUTION WITH WATER.

BY OLAF BERGEIM AND P. B. HAWK.

Received February 20, 1913.

Many investigations have been made on the influence of variations in the concentration of enzymes, of their substrates, and of electrolytes, on the rate of the reaction. Very little work has, however, been done directly on the effect of simultaneous decreases of all three of these, that is, of dilution. For example in the case of the amylases, as was first

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[1] Hans Meyer and Krczmar, *Monatsh.*, 19, 715 (1898).