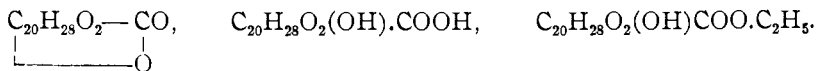


Zeisel's method. Found: 10.78 and 11.50 per cent. of  $C_2H_5O$ . Calculated: 11.54 per cent. of  $C_2H_5O$ . The ester forms an acetyl derivative, but this and several other derivatives of marrubiin will be reported upon in my next paper. The results of the investigation so far show that marrubiin is a lactone behaving like a  $\gamma$ -lactone in that it easily takes up a molecule of water and changes to a hydroxy acid. The formulae of marrubiin, marrubic acid and ethyl marrubate can therefore be written as follows:



The investigation is continued.

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## DECOMPOSITION CURVES OF SOME NITROCELLULOSES OF AMERICAN MANUFACTURE.<sup>1</sup>

BY OSWIN W. WILLCOX.  
Received November 11, 1907.

In the course of a study of the test proposed by Obermuller<sup>2</sup> for the stability of nitrocellulose, it was observed that the rate of decomposition of an ordinary collodion cotton during a given period of time depended on whether or not the gaseous products of decomposition had been allowed to remain in contact with the sample during previous periods. As the Obermuller apparatus is perhaps the most accurate and convenient means yet devised for following quantitatively the progress of the decomposition of a nitrocellulose at temperatures below its ignition point, some of the results obtained are deemed of interest.

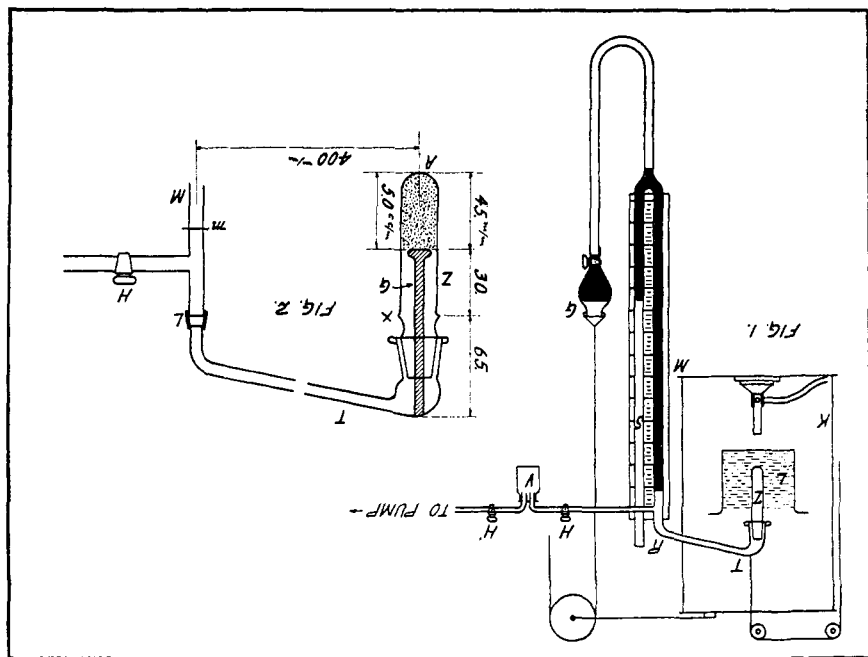
Obermuller's test is essentially as follows: A weighed quantity of the nitrocellulose to be tested is placed in a glass tube, which is then evacuated by means of a good air pump. When the air has been removed as much as possible, the tube is plunged into a bath previously brought to a standard temperature, which is maintained constant throughout the duration of the test. The nitrocellulose in the tube immediately begins to decompose and to give off gaseous products; the tube being in connection with a mercury manometer, the rate at which the products of decomposition are evolved is measured by the increase of pressure shown by the manometer. This rate will naturally be greater for nitrocellulose of poor stability and less for nitrocellulose of good stability. Working at a standard temperature of  $140^\circ C.$ , and with a tube which, with its connections, had a volume of 37 cc., Obermuller

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

<sup>2</sup> Mittheilung aus dem Berliner Bezirksverein des Vereins deutscher Chemiker, October 11, 1904.

found that one gram of a stable nitrocellulose does not cause in one hour a greater increase of pressure than 100 mm. of mercury.

The apparatus employed is diagrammatically shown in Figs. 1 and 2, which are copied from Obermuller's paper. The decomposition tube



Figs. 1 and 2.

Z (Fig. 1) is of glass and of about 12 cc. capacity; the top of Z is ground to fit the larger end of T, by means of which it is connected to the manometer M. Behind the manometer is a scale S. By means of the side tube R the decomposition tube can be put in communication with the air pump. V is a glass bottle, on either side of which is a glass stopcock (H and H'). The lower part of the manometer is connected with the mercury reservoir G. The bath, L, which may consist of a saturated solution of calcium chloride, or, better, of oil, such as is used in the cylinders of locomotives, serves to heat the tube Z. The sheet-iron case K, which is provided with a window of heavy glass, serves to protect the operator from possible explosions. In Fig. 2 is shown an enlarged sketch of the tube Z and its connections. G is a glass rod sealed by its upper end to T; the object of this rod is to hold the nitrocellulose in place in the lower end of Z. X is a mark 1 cm. under the cap.

The method of procedure adopted in this study is as follows: Exactly 2 grams of the nitrocellulose previously dried by heating for 1 hour at  $100^{\circ}$  were placed in the decomposition tube Z; any nitrocellulose

adhering to the walls of the tube were swept down by means of a small wad of pure dry absorbent cotton, which was allowed to remain in the tube during the heating. The tube was then fitted in place and evacuated as completely as possible, usually down to an internal pressure of less than 5 mm. of mercury. The bath having been brought to 140° the positions of the mercury in both limbs of the manometer were noted, all stopcocks were closed and the tube lowered into the bath up to the mark X, the time being noted at the same instant. Exactly 15 minutes from the time of immersing the tube, the surface of the mercury in the left limb of the manometer was brought back to its original position and the rise of the mercury in the right limb was noted; and this was repeated at intervals of 15 minutes until four such readings had been taken. The accumulated gases were now pumped out and a vacuum maintained in the tube for 15 minutes. At exactly 75 minutes from the time of beginning all stopcocks were again closed and the gaseous products of decomposition allowed to accumulate for a period of 15 minutes. The pressure developed during these 15 minutes was read, the tube again kept vacuous for 15 minutes, and so on alternately for 5 hours from the time of beginning. For convenience in discussion, the whole time of heating may be regarded as divided into periods of 15 minutes each. During the first four periods the gases were allowed to accumulate in the tube and to exert pressure; after the first hour the gases were being continually withdrawn during the odd periods, whereas they were allowed to accumulate during the even periods. The procedure followed during the first hour will be referred to as "test with increasing initial pressure," and that followed after the first hour as "test with constant initial pressure." All readings of pressure are given as millimeters of mercury per gram of substance. The data obtained are tabulated in Table I.

TABLE I.  
Pressure in mm. of mercury per period of 15 minutes.

No. of sample.	Test with increasing initial pressure.				Test with constant initial pressure.							
	1st.	2nd.	3rd.	4th.	6th.	8th.	10th.	12th.	14th.	16th.	18th.	20th.
2920	20.3	23.9	28.7	32.9	27.8	28.6	30.6	31.0	33.5	33.0	33.5	34.0
3831	18.7	23.4	27.7	33.0	27.7	28.7	30.6	31.3	33.7	32.7	34.5	34.5
3883	18.6	22.2	27.8	32.0	27.6	28.2	30.3	30.6	32.2	32.5	33.0	33.5
3863	21.0	29.5	35.0	42.7	38.0	39.7	41.8	43.3	45.7	45.7	47.0	47.5
3607	21.9	24.5	28.7	34.2	31.5	33.5	34.1	34.5	36.7	36.2	39.0	38.0
3608	19.2	20.9	24.6	29.1	25.5	27.0	28.1	29.1	29.7	31.7	31.5	32.5
3609	18.1	22.2	25.8	25.8	29.4	26.1	28.5	28.3	29.5	29.7	32.0	32.0

The samples of nitrocellulose here reported on represent the product of the principal factories of the United States. They are "decanitrocelluloses" of about 12.60 per cent. nitration and 99 per cent. solubility in ether alcohol.

The figures at the top of the columns in Table I are the numbers of the periods, of 15 minutes each, during which the gases were allowed to accumulate (it will be remembered that a vacuum was maintained in the tube during the odd periods). The results are also plotted in the accompanying curves. An examination of the figures given in Table

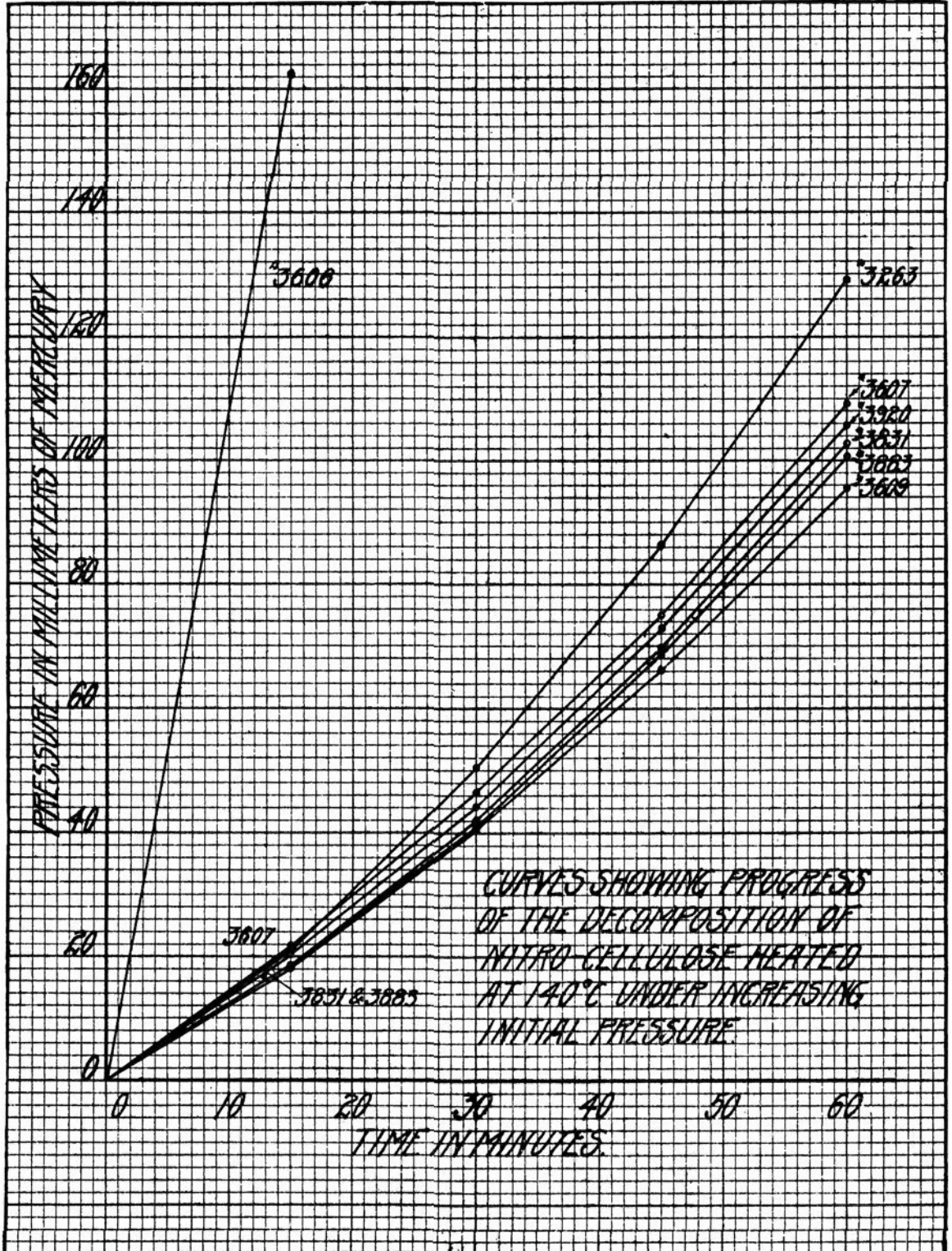


Fig. 3.

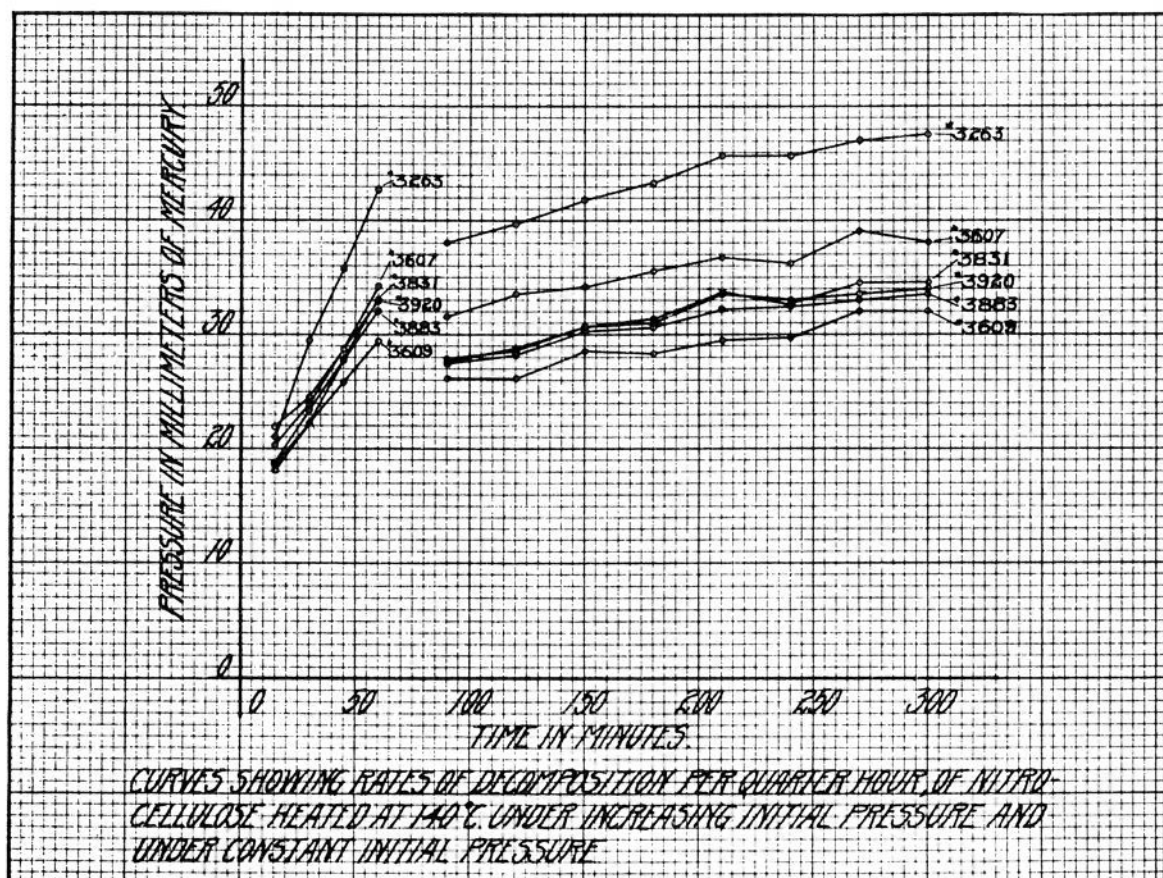


Fig. 4.

I will show that the course of the decomposition in "test with increasing initial pressure" and in "test with constant initial pressure" follows different laws. In the case of sample No. 3831, for example, the quarter hourly increase of pressure in the first period is 18.7 mm., in the second 23.4 mm., in the third 27.7 mm., and in the fourth 33.0 mm., an average constant difference of about 4.5 mm. By the aid of this law of increase it may be calculated that during the sixth period the increase of pressure would be 42 mm., if the gases were allowed to accumulate in the tube without interruption. The calculated rate for the sixth period was found by experiment to be the actual rate under the condition named. If, however, a vacuum be maintained in the tube during the fifth period, then the increase of pressure during the sixth period is not 42 mm., but only 27.7 mm., a difference of 14.3 mm. The difference in the rates of increase of pressure under the two conditions measures the catalytic effect of the presence of the gaseous products of decomposition on the speed of the reactions of decomposition. It may be noted that while removal of the gases lowers the "decomposition pressure" of the heated nitrocellulose it is not restored to the original value; the initial decomposition pressure gradually rises with the time of heating.<sup>1</sup>

<sup>1</sup> At the same time the heated nitrocellulose is being transformed into a modification soluble in absolute alcohol. A separate report, with quantitative data, will be made on this subject in the future.



The results reported in Table I were obtained by working at a constant volume of 30 cc. It is obvious that as the volume of the tube and its accessories determines the concentration of the gaseous products of decomposition, the rate of increase of pressure will vary with this volume. To deduce the volume relations of the test a number of exper-

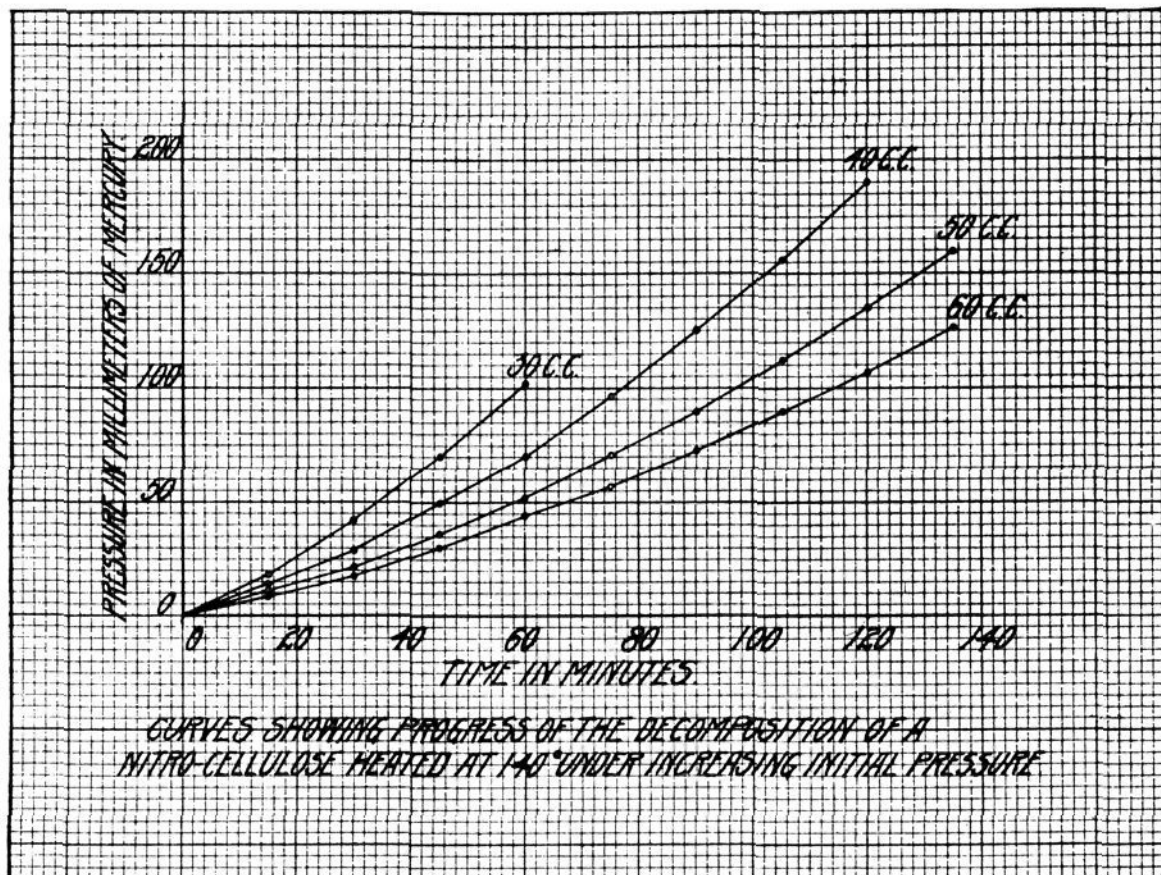


Fig. 5.

iments were made on sample No. 3831. The total volume of the apparatus as far as the glass cock H' was measured and found to be 60 cc. On leaving H open during a determination, the gases would exert a pressure corresponding to this volume. By adding 10 cc. of mercury to the glass bottle V, the volume could be reduced to 50 cc., another 10 cc. of mercury would reduce it to 40 cc., and so forth. The pressures obtained by working at the volumes 30 cc., 40 cc., 50 cc., and 60 cc. are given in

TABLE II.

## OBERMULLER TEST AT DIFFERENT VOLUMES.

Pressure in mm. of mercury per period of 15 minutes.

Volume in cc.	Test with increasing initial pressure.				Test with constant initial pressure.							
	1st.	2nd.	3rd.	4th.	6th.	8th.	10th.	12th.	14th.	16th.	18th.	20th.
30	18.7	23.4	27.7	33.0	27.7	28.7	30.6	31.3	33.7	32.7	34.5	34.5
40	12.5	17.0	19.5	22.0	21.0	21.0	23.0	25.0	24.5	24.5	26.5	25.5
50	10.0	12.5	15.0	16.0	15.5	17.0	17.5	17.5	18.5	19.5	20.5	21.0
60	8.0	9.5	12.0	13.5	13.5	14.6	15.5	15.0	15.5	15.5	16.5	16.0

Table II, and are plotted in Figs. 5 and 6. As was to have been expected, the pressure increases as the volume decreases. During a given period of heating the evolution of gaseous products of decomposition in "test with constant initial pressure," is constant. The equation

$$PV = K$$

where P is the pressure developed during a period, V the volume, and K a constant, holds for all volumes between 30 cc. and 60 cc. The av-

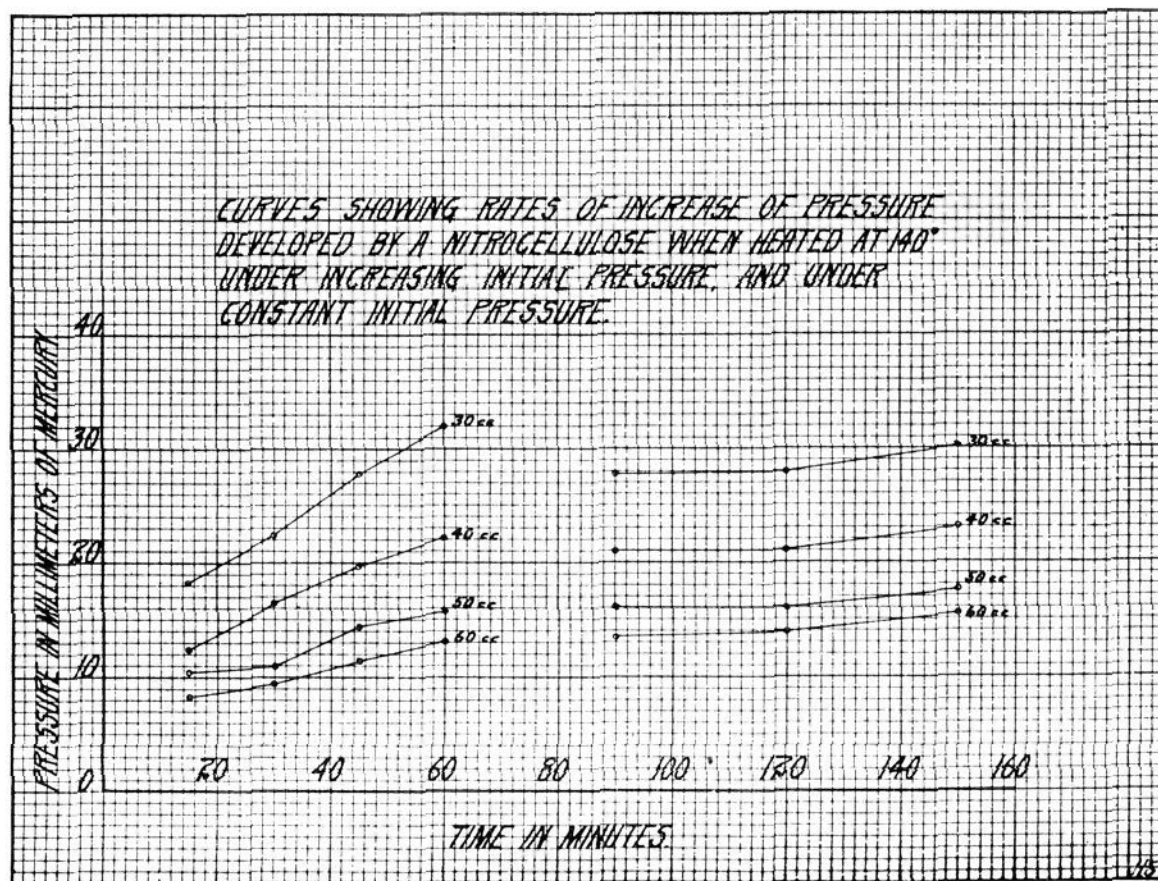


Fig. 6.

erage values of K are plotted in the curve shown in Fig. 7. This curve represents as nearly as may be, the course of the decomposition of a nitrocellulose when heated in a vacuum. In "test with increasing initial pressure" as the volume decreases the pressure increases according to a law which can be stated as follows: If the original volume be 60 cc., and if this volume be successively decreased by a constant quantity, then the pressure developed in one hour at any other volume can be found from the equation

$$P_n = P_{60} + \frac{n(n+1)}{2} C,$$

where P is the pressure expressed in millimeters of mercury, n the number of times the volume has been decreased by a constant quantity, and C a constant. For stable American collodion cotton  $P_{60}$  is about

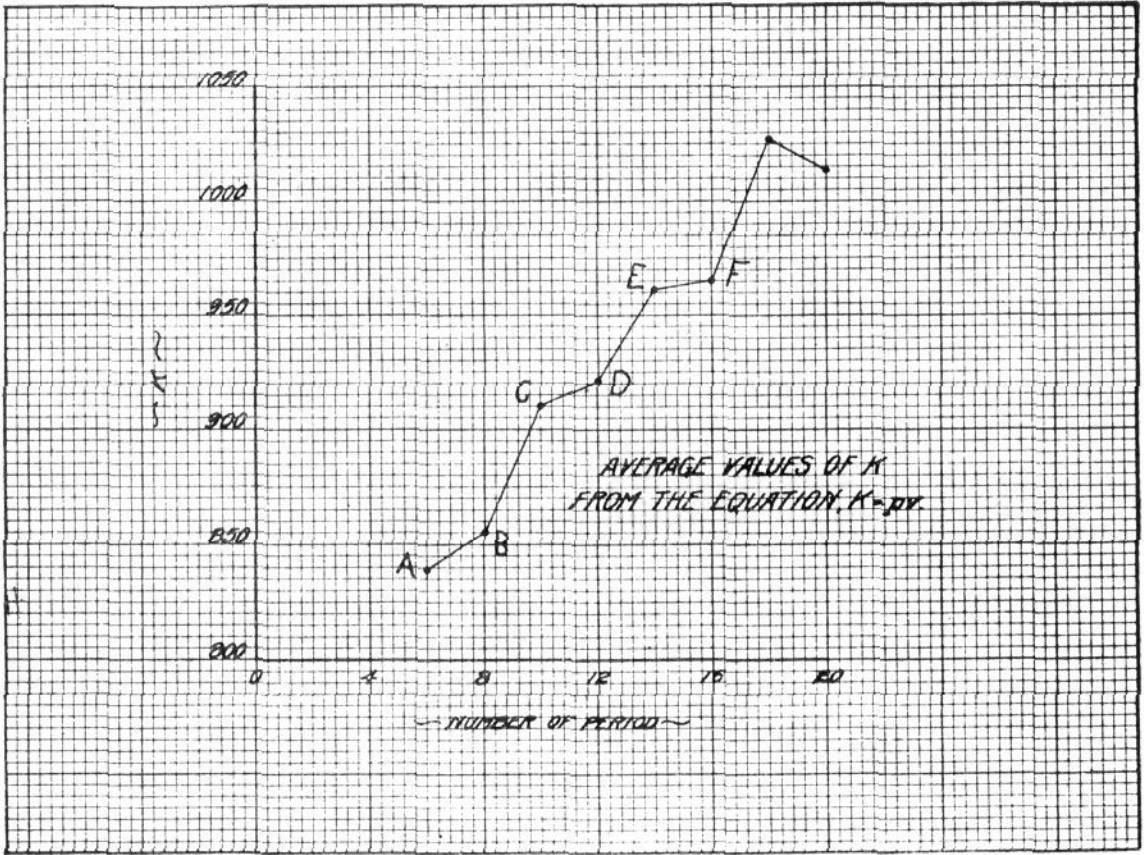


Fig. 7.

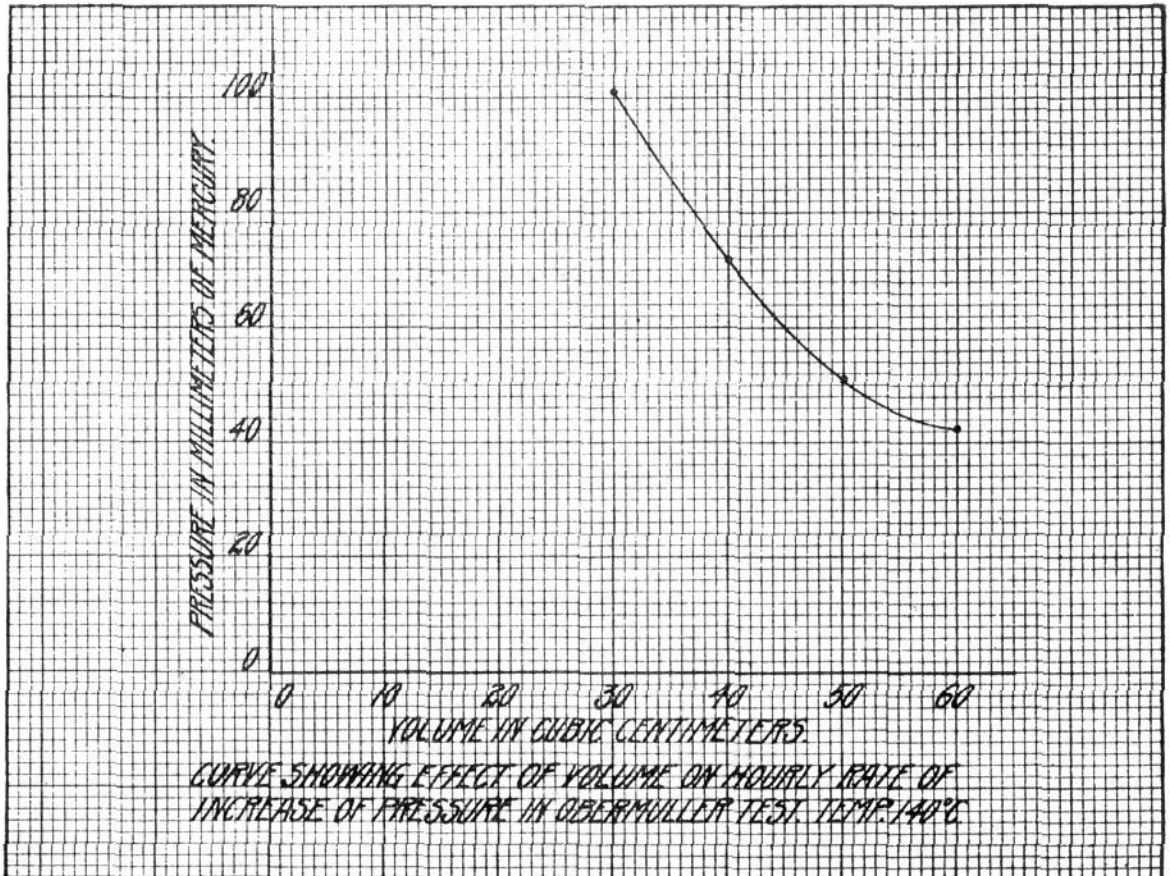


Fig. 8.



43 mm. and, under the conditions above described, C is about 9. The above equation has been proven for volumes between 30 cc. and 60 cc.

The values of  $P_{\infty}$ , when plotted, give the rectangular hyperbola shown in Fig. 8.

A noteworthy feature of the curves showing the rate of increase of pressure developed by a nitrocellulose in "test with constant initial pressure" is that they are not straight lines nor smooth curves, but are made up of oblique and horizontal lines. This is discernible in the curves shown in Fig. 4 and is well marked in Fig. 7, wherein are plotted the average values of  $K$ , calculated from the data given in Table II. The step-like character of these curves reminds one of the curve representing the progress of the dehydration of a hydrated salt like  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , which can be transformed into lower hydrates, each having its own vapor pressure. The resemblance is sufficient to suggest the explanation that a given sample of nitrocellulose when heated at  $140^\circ$  has a characteristic decomposition pressure which is represented by the first approximately horizontal portion of the curve (A B, Fig. 7). As the heating progresses a new phase or component appears and adds its decomposition pressure or accelerative action to the previous one, giving the new horizontal section C D. The rate of increase of pressure represented by this part of the curve remains fairly constant until a new phase or component appears, whence results the horizontal section E F. It appears to be characteristic of nitrocellulose of good stability that the curves obtained in "test with constant initial pressure" have this step-like character plainly developed. In Fig. 9 the transition between two

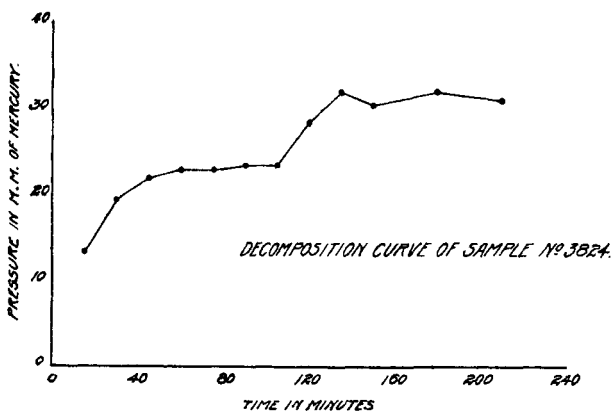


Fig. 9.

adjacent horizontal sections is well brought out. The curve shown in this figure was taken from the record of a different sample, No. 3222; in this case a fresh portion was taken for each pressure determination,

and the tube was kept evacuated until just before the period for which it was desired to measure the decomposition pressure of the material.

According to Saposhnikov<sup>1</sup> the relation of velocity of decomposition of a nitrocellulose to temperature for temperatures between 125° and 140°, and between 145° and 155° can be expressed by the equations  $\left(\frac{dv}{dt}\right)_{\text{max.}} = 24.6 + 0.201t$  and  $\left(\frac{dv}{dt}\right)_{\text{max.}} = 136.5 + 0.985t$ , respectively; the ratio of reaction velocity to temperature within each of these ranges of temperature can therefore be represented by a straight line. Solving the two equations simultaneously, 143° is indicated as the temperature at which these two lines will intersect. At this temperature

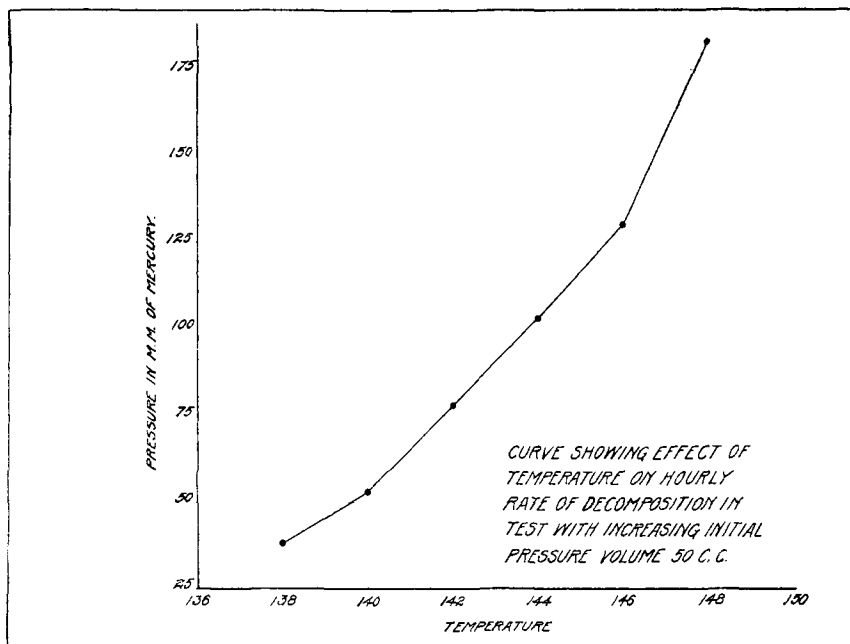


Fig. 10.

a sharp change in the ratio takes place in either direction. Before I became aware of Saposhnikov's work I had thoroughly studied the temperature relations of the Obermuller test, employing a temperature interval of 2° instead of 5°, as employed by Saposhnikov. My results between 138° and 148° are as follows (volume, 50 cc.):

Temperature:	138°	140°	142°	144°	146°	148°
Pressure (mm.)	38	53	77	103	130	183

From these data are obtained the curve shown in Fig. 10. Instead

<sup>1</sup> Russ. Phys. Chem. Soc., 38, 1186 (1906); reviewed by H. M. Gordin in Chemical Abstracts, May 20, 1907.

of one sharp change in the rate of decomposition at  $143^{\circ}$  there are here shown two such breaks, one at  $140^{\circ}$  and one at  $146^{\circ}$ . As the Obermuller apparatus uniformly gives concordant results within  $\pm 2$  mm. the position of the curve is sensibly free from experimental error.

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[CONTRIBUTION FROM THE AGRICULTURAL CHEMICAL LABORATORY OF THE WISCONSIN EXPERIMENT STATION.]

## VARIATIONS IN THE AMOUNT OF CASEIN IN COW'S MILK.

E. B. HART.

Received November 11, 1907.

There is a general belief among dairymen and some dairy chemists that casein and fat are present in milk in very constant relative proportions; that given the percentage of fat in milk, the percentage of casein can be directly calculated by rule. This rule was formulated by Van Slyke<sup>1</sup> and is based on averages of numerous analyses made at the New York Agricultural Experiment Station. The rule is to be applied especially to milks ranging from three to four and one-half per cent. of fat and is stated as follows: to find the per cent. of casein in milk when the per cent. of fat is known, subtract 3 from the per cent. of fat in milk, multiply the result by 0.4 and add the result to 2.1. The limitations placed on the rule as applicable to milks containing but from three to four and one-half per cent. of fat led the writer to inquire how applicable it might be to milks of higher fat content. Hill,<sup>2</sup> as early as 1890, showed that in individual cows the proportion between fat and casein is widely different. He, however, obscured this important fact by conclusions based on averages of many milk analyses. His conclusion was that normal milks, whether rich or poor, have on an average, one-fourth as much casein as total solids, though he further says that single samples may depart widely from this standard.

Shuttleworth,<sup>3</sup> from work on individual cows, showed that a considerable variation in the proportion of casein to fat existed among different animals, and that a ratio established for one period of lactation in any single animal may not be the same as the ratio found at some other period for the same animal.

*A priori* there seems to be no good reason why we should expect a definite quantitative relation between these two constituents of milk. They are entirely unlike in chemical constitution and their elaboration has been along different lines of synthesis. If we could suppose that they

<sup>1</sup> Modern Methods of Testing Milk," p. 192.

<sup>2</sup> Fourth Annual Rept. Vt. Agr. Exp. Sta.

<sup>3</sup> Rept. of Ontario Exp. Farm, 1895.