These results, establishing as they do the fact that methane and ethane are soluble in fuming sulphuric acid, are not without importance in their bearing toward gas analysis. A number of experiments were tried to determine the amount of absorption of each gas that took place in short intervals of time. After twenty-five per cent. of the methane obtained from natural gas had been absorbed, the residue was tested by measuring its absorption each hour. The results showed this absorption to be very slight, less than one-tenth cc. per hour. In the case of ethane, however, after over sixty per cent. had been absorbed, a similar series of experiments gave an average hourly absorption of 0.25 cc. equivalent to 0.60 per cent. of the ethane present.

In ordinary technical gas analysis, therefore, when the gas contains methane but no ethane, the absorption in the fuming sulphuric acid could be allowed to continue for an hour if necessary without much danger of serious error. But if ethane is present, fifteen minutes is the probable maximum of safety, and in any case the safest course to follow, especially in the case of an unknown gas, would be to shorten the time of contact with fuming sulphuric acid to the lowest possible limit.

LAFAYETTE, IND., October, 1898.

## THE VELOCITY OF THE REACTION BETWEEN SILVER ACETATE AND SODIUM FORMATE. A REACTION OF THE THIRD ORDER.[1]

BY ARTHUR A. NOYES AND GEORGE T. COTTLE.
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### I. OBJECT OF THE INVESTIGATION.

THE investigations hitherto made of the velocities of those reactions in which two or more molecules of a substance enter have not yielded results of a general character. In many cases the velocity has been found proportional simply to the concentration of the substance, while in others it has been found proportional to that power of its concentration which corresponds to the number of its molecules entering into the reaction, as theoretical considerations would appear to demand. Thus, for ex-

[1] Read before the Boston meeting of the American Chemical Society, August 25, 1898.

ample, the reactions between iron salts and potassium chlorate,[1] between hydrogen peroxide and potassium iodide[2], and between potassium bromate and potassium iodide[2], in the presence of an excess of acid, are all simple reactions of the second order, although three or more molecules take part in the chemical change. In two cases, on the other hand, have the number of reacting molecules shown their influence; namely, that of the polymerization of cyanic acid,[3] and that of the reaction between stannous chloride and ferric chloride,[4] both of which, in correspondence with the number of reacting molecules, follow the law of the third order.

Further investigations of such reactions are therefore necessary. A new, and, it would seem, a suitable, example is the reaction between silver acetate and sodium formate, and we have, therefore, measured its velocity. The reaction is expressed by the following equation :

$$2AgC_2H_3O_2 + HCO_2Na = 2Ag + CO_2 + HC_2H_3O_2 + NaC_2H_3O_2$$

or, more correctly, according to the dissociation theory :

$$2\overset{+}{Ag} + H\overset{-}{CO_2} = 2Ag + CO_2 + \overset{-}{H}.$$
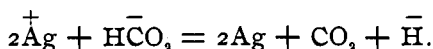
Thus it is a simple trimolecular reaction and should apparently follow the law of the third order, if any such reaction does so. We have selected a salt of formic acid in place of the acid itself and a silver salt of a very weak acid, in order to eliminate as far as possible the catalytic effect of the hydrogen ions.

## II. DESCRIPTION OF THE EXPERIMENTS.

The sodium formate and the silver acetate used were prepared by recrystallizing the commercial salts, their purity being assured by qualitative tests. An exactly normal solution of the first, and a nineteenth normal of the second were made. The strength of the former solution was determined by addition of hydrochloric acid to a known amount in a platinum dish, evaporating to dryness, and weighing the residue ; that of the latter by titration with potassium thiocyanate.

[1] Hood : *Phil. Mag.*, (5), 6, 371; 8, 121 ; 20, 323 ; Noyes and Wason : *Ztschr. phys. Chem.*, 22, 210.
[2] Noyes and Scott : *Ztschr. phys. Chem.*, 18, 118.
[3] Van't Hoff : Etudes de Dynamique Chimique, S. 90.
[4] Noyes : *Ztschr. phys. Chem.*, 16, 546.

As the velocity of the reaction is very small at ordinary temperatures, we carried on the experiments at 100°.   For this purpose we constructed a steam thermostat out of a cylindrical tin can.    In the cover, before it was soldered on, were cut one small hole, for a ball condenser, and five large holes, two inches in diameter, provided with quarter-inch tin collars covered with rubber tubing.    In these were then placed large 225 cc. test-tubes containing the measured amounts of silver acetate solution and of water.    In the cases where the concentration of the silver solution was 0.100 normal, solid silver acetate was weighed directly into the tube and the necessary amount of water added, as so strong a solution of the salt cannot be prepared in the cold. Each of the large tubes was then fitted with a cork through which were passed a small twenty-five cc. test-tube containing the required amount of formate solution and of water, a thermometer, an efficient glass stirrer, and tubes for blowing out samples.    The water in the bottom of the thermostat was kept boiling constantly, and when the temperature of the solution had become quite constant, the bottom of the small tube was broken by a glass rod, the two solutions immediately mixed by violent stirring, and the time (to the second) noted.    At definite moments samples of the mixture were blown out into measured amounts of ice-cold standardized potassium thiocyanate solution, thus instantly stopping the reaction.    As the flasks containing the thiocyanate were weighed before and after addition of the sample, the amount of the latter was easily determined.    The end-point was then determined after filtration by titration with silver nitrate and potassium thiocyanate solutions, using ferric alum as an indicator. Thus the silver content of the mixture and the progress of the reaction were ascertained.

### III. EXPERIMENTAL RESULTS AND VELOCITY CONSTANTS.

The results of the experiments and the calculated velocity-constants are found in the following tables.   All experiments were carried out at the temperature of water boiling under atmospheric pressure.   $A$ expresses the original concentration of the sodium formate, and $B$ that of the acetate.   Under $t$ are found the time in minutes reckoned from the moment of mixing.   Under $(B-x)$, and $(B-x)_2$ are given the concentrations of the silver

acetate found in two separate experiments after the time $t$, and under $B—x$ will be found the average of these results.    Under $C_2$ and $C_3$ are given the constants of the second and of the third order respectively which occur in the equations :

$$\frac{dx}{dt} = C_2(A—x)(B—x) \text{ and}$$

$$\frac{dx}{dt} = C_3(A—x)(B—x)^2.$$

They are calculated, of course, from the corresponding integrated equations.[1]  At the foot of each column of the $C_2$ values, is given the value, obtained by interpolation, corresponding to the time when the reaction is one-half completed.    Under each column of $C_3$ values, the mean of the same is given.

FIRST SERIES.

$A = 0.100$ ; $B = 0.100$.

| $t$. | $(B—x)_1$. | $(B—x)_2$. | $B—x$. | $C_2$. | $C_3$. |
|---|---|---|---|---|---|
| 2 | 0.06694 | ...... | 0.06694 | 2.57 | 30.8 |
| 4 | 0.05334 | ...... | 0.05334 | 2.19 | 31.3 |
| 6 | 0.04684 | ...... | 0.04684 | 1.89 | 29.6 |
| 9 | 0.03784 | ...... | 0.03784 | 1.83 | 33.3 |
| 14 | 0.03235 | ...... | 0.03235 | 1.61 | 30.6 |
|  |  |  |  | 2.05 | 31.1 |

SECOND SERIES.

$A = 0.100$ ; $B = 0.050$.

| 2 | 0.03774 | 0.03776 | 0.03775 | 1.51 | 34.9 |
|---|---|---|---|---|---|
| 4 | 0.03090 | 0.03080 | 0.03085 | 1.35 | 35.1 |
| 7 | 0.02455 | 0.02425 | 0.02440 | 1.20 | 35.9 |
| 11 | 0.01959 | 0.01958 | 0.01959 | 1.04 | 35.6 |
| 17 | 0.01519 | 0.01483 | 0.01501 | 0.91 | 36.7 |
|  |  |  |  | 1.22 | 35.6 |

THIRD SERIES.

$A = 0.050$ ; $B = 0.100$.

| 2 | 0.08112 | 0.08093 | 0.08103 | 2.67 | 29.9 |
|---|---|---|---|---|---|
| 4 | 0.07180 | ...... | 0.07180 | 2.49 | 30.2 |
| 7 | 0.06395 | ...... | 0.06395 | 2.36 | 31.2 |
| 11 | 0.05920 | ...... | 0.05920 | 2.11 | 29.7 |
| 16 | 0.05625 | ...... | 0.05625 | 1.88 | 28.0 |
|  |  |  |  | 2.56 | 29.8 |

[1] Cf. Fuhrmann: *Ztschr. phys. Chem.*, 4, 89.

FOURTH SERIES.

$A = 0.050$ ; $B = 0.050$.

| $t$. | $(B-x)_1$. | $(B-x)_2$. | $B-x$. | $C_2$. | $C_3$. |
|---|---|---|---|---|---|
| 3 | 0.04019 | 0.04047 | 0.04033 | 1.60 | 35.8 |
| 8 | 0.03145 | 0.03173 | 0.03159 | 1.46 | 37.6 |
| 16 | 0.02473 | 0.02463 | 0.02468 | 1.28 | 38.8 |
| 25 | 0.02033 | 0.02066 | 0.02048 | 1.16 | 37.6 |
| 45 | 0.01629 | ...... | 0.01629 | 0.92 | 37.4 |
| 80 | 0.01250 | ...... | 0.01250 | 0.75 | 37.5 |
| | | | | 1.29 | 37.4 |

FIFTH SERIES.

$A = 0.050$ ; $B = 0.0250$.

| 3 | 0.02192 | ...... | 0.02192 | 0.91 | 38.7 |
|---|---|---|---|---|---|
| 5 | ...... | 0.02004 | 0.02004 | 0.94 | 40.2 |
| 11 | 0.01634 | ...... | 0.01634 | 0.85 | 43.0 |
| 12 | ...... | 0.01579 | 0.01579 | 0.85 | 43.6 |
| 23 | 0.01194 | 0.01190 | 0.01192 | 0.76 | 45.8 |
| | | | | 0.77 | 42.3 |

SIXTH SERIES.

$A = 0.0250$ ; $B = 0.050$.

| 10 | 0.03766 | ...... | 0.03766 | 1.49 | 37.3 |
|---|---|---|---|---|---|
| 25 | 0.03136 | ...... | 0.03136 | 1.44 | 38.6 |
| 45 | 0.02840 | ...... | 0.02840 | 1.27 | 37.3 |
| 80 | 0.02653 | ...... | 0.02653 | 1.08 | 34.4 |
| | | | | 1.49 | 36.4 |

SEVENTH SERIES.

$A = 0.0250$ ; $B = 0.0250$.

| 10 | 0.02024 | 0.02009 | 0.02017 | 0.96 | 42.9 |
|---|---|---|---|---|---|
| 25 | 0.01626 | 0.01623 | 0.01624 | 0.86 | 43.8 |
| 45 | 0.01297 | 0.01276 | 0.01286 | 0.84 | 49.3 |
| 80 | 0.01140 | 0.01120 | 0.01130 | 0.61 | 39.0 |
| | | | | 0.67 | 43.7 |

### IV. DISCUSSION OF THE RESULTS.

Let us now consider the significance of the experimental results. In order to ascertain the order of a reaction and the influence of the individual substances upon its velocity, there are, as is well known, two different methods.[1] The first of these methods consists in determining the degree of the differential equation whose constants show the least variation during a sin-

[1] Cf. Noyes: *Ztschr. phys. Chem.*, **18**, 119; **22**, 215.

gle experimental series.   A brief glance at the preceding tables
suffices to show  that, in every series, the values of $C_2$ exhibit a
constant,  and as a rule  very considerable,  diminution during
the progress of the reaction.   On the other hand, the tables also
show  that the  values of  $C_3$ remain  practically constant.   The
reaction, judged  by this  method, is  therefore one  of  the third
order.

The second method of determining the order of a reaction con-
sists in degree of the equation whose constants retain nearly
the  same  value  in  *independent*  series  of  experiments  with
very different original concentrations.   This method is much
more reliable  than  the  former, because  the  effect of disturb-
ances, such for example as the influence of  the products of the·
reaction upon the velocity, in comparison with the much greater
effect of the large variations in the original concentration, becomes
of no consequence.   In order to show more distinctly the results
obtained by the application of this second method to the reaction
considered  here, we  present the following  table, in  which the
comparable values of the  constants of both  orders derived from
the seven experimental  series  are  given.    Under $C_3$  the mean
values  are  shown, while under $C_2$ the  values  are  given which
correspond to the state  of the reaction in  which one-half of the
substance present in smallest amount has undergone change.

| Series. No. | Normal concentration of | | $C_2$. | $C_3$. |
|---|---|---|---|---|
| | Sodium formate. | Silver nitrate. | | |
| I | 0.100 | 0.100 | 2.05 | 31.1 |
| 2 | 0.100 | 0.050 | 1.22 | 35.6 |
| 3 | 0.050 | 0.100 | 2.56 | 29.8 |
| 4 | 0.050 | 0.050 | 1.29 | 37.4 |
| 5 | 0.050 | 0.025 | 0.77 | 42.3 |
| 6 | 0.025 | 0.050 | 1.49 | 36.9 |
| 7 | 0.025 | 0.025 | 0.67 | 43.7 |

It is evident that the values of  $C_3$ in all seven  of  the series
are  approximately the  same, while  those of  $C_2$ vary about  280
per cent., which proves  that the reaction is essentially one of the
third order, and  that its velocity is  nearly  proportional  to the
concentration of  the sodium  formate and  to the  square of  the
concentration of  the silver acetate.   In the case of this reaction,
therefore, the two methods for the  determination of the order of
a reaction, lead to the same conclusion.

Still, we must not leave unmentioned the fact that the proportion-ality between the velocity and the square of the concentration of the silver acetate is not absolutely exact. While the change of the original concentration of the formate exerts no definite influ-ence upon the constants of the third order, yet, as will be seen from the last table, there occurs with every diminution of the original concentration of the silver salt, a slight, but still unmistakable, increase in the values of the constants $C_3$. As to the cause of this phenomenon, nothing can be said with certainty. It is not improbable, however, that the greater velocity in the more dilute solutions depends upon the greater dissociation of the silver salt, it being then assumed that only the silver ions are capable of reacting.

### V. SUMMARY.

By this research it is established that the reaction between sodium formate and silver acetate proceeds with a velocity which is proportional to the concentration of the former salt, and nearly proportional to the square of the concentration of the lat-ter. As this reaction, according to prevailing molecular ideas, takes place between one molecule of the formate (or of its anion) and two molecules of silver acetate (or of its silver ion), its ob-served velocity is in accordance with the theoretical require-ments, and it furnishes a new confirmation of the influence of the number of the molecules taking part in reactions.

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## COUMARIN AND VANILLIN, THEIR SEPARATION, ESTIMATION AND IDENTIFICATION IN COM-MERCIAL FLAVORING EXTRACTS.[1]

BY WILLIAM H. HESS AND ALBERT B. PRESCOTT.

IT is a common practice in preparing an extract of vanilla from vanilla beans, to introduce also, as a lower-priced material, a portion of tonka beans. This makes a cheaper article and one that is generally popular with consumers. It is understood, how-ever, to be an inferior article when compared with the genuine, and it can no longer be correctly labeled ''Vanilla Extract.'' Under this name the presence of tonka extract constitutes an adulteration and hence the separation, identification, and esti-