THE ACTION OF BASES ON FORMALDEHYDE. PART 1. THE FORMATION OF SALTS OF FORMIC ACID FROM FORMALDEHYDE.

and

POLYMOLECULAR CHEMICAL REACTIONS.

by

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THE ACTION OF BASES ON FORMALDEHYDE.

PART 1.

THE FORMATION OF SALTS OF FORMIC ACID FROM FORMALDEHYDE.

Formaldehyde in alkaline solution undergoes two distinct transformations - on the one hand, condensation to sugars, and on the other, conversion to formates. The latter is the more general reaction, and its study forms the subject of this paper.

When formaldehyde comes into contact with strong bases at higher temperatures formates and methyl alcohol are always produced 1), and even at ordinary temperatures this change can be detected. 2) The similar reaction with benzaldehyde is perhaps the best parallel. 3) H. and A. Euler 4) appear to be the only investigators who have studied in detail the formation of formates from formaldehyde. These authors draw the following conclusions from their work:

1) Formate formation is a simple cleavage process without oxidation, since the reaction takes place as quickly in an atmosphere of hydrogen, as in oxygen.
2) Formaldehyde/

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1) Loew, Ber., (1888), 21, 270.
2) Delépine, Bull. Soc. chim., (1897), 17, 939.
3) Pomeranz, Monatsh., (1900), 21, 389.
4) Ber., (1905), 38, 2551; Ber., (1906), 39, 36.

2) Formaldehyde behaves as a weak acid, its dissociation constant being about 1.4×10^{-14} at 0°C. It forms salts with bases.
3) Formates are probably formed from these salts of formaldehyde.
4) Even when no sugar formation takes place, the dissolved bases possess a specific formate producing power. Sodium hydroxide and barium hydroxide behave very similarly. Calcium hydroxide, with regard to both the speed and method of action, exhibits an irregular behaviour which leads one to suspect the formation of an "active" calcium formaldehyde complex.

Some of these conclusions are of doubtful accuracy. The present research was undertaken, in the first place, to show whether or not the various bases act in the same way, and, secondly, to elucidate, if possible, the method of action of the various bases. To compare the action of the bases, experiments were performed to find the rate at which they brought about the transformation of formaldehyde into formates. From a study of the velocity constants obtained with varying base and formaldehyde concentrations, attempts were made to settle the mode of action of the different bases.

SECTION 1, (Experimental).

Preparation of pure, methyl-alcohol-free Formaldehyde Solutions.

Several methods are known for the preparation of formaldehyde solutions free from methyl alcohol [1], and salts [2]. Those used in the present research were prepared by a new method, which was found to be both rapid and efficient. The commercial 40% solution, diluted with about half its volume of water, was put into a steam distillation apparatus, and made distinctly alkaline with caustic soda. After being heated up, it was subjected to steam distillation. The alcohol came over first, and was followed by polymerised aldehyde, which solidified on the sides of the condenser. When about 250cc. of distillate had been rejected, practically no more polymer appeared, and the aldehyde solution was collected. This always showed a very slight acid reaction. An attempt to obtain a neutral distillate by keeping the solution in the distilling flask slightly alkaline by the slow addition of Sodium hydroxide failed, since, as long as alkali was added, polymerised aldehyde came over.

Estimation of the Formaldehyde Content of the Solutions.

Many methods have been suggested for the estimation of formaldehyde in solution. Fresenius/

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[1] J. Chem. Soc., (1925), 127, 26.
[2] Arb.a.d.Kais.Gesundheitsamte, (1905), 22, 584.

Fresenius and Grünhut[1] have critically tested several of these, and have shown the accuracy of Romijn's iodometric method[2]. Smith[3], in a comparative study of methods of determining formaldehyde, came to the conclusion that Romijn's method gives good results for dilute solutions. Auerbach[4] favoured the sodium sulphite method for concentrated solutions, but advised Romijn's method for very dilute solutions, or small quantities of moderately concentrated solutions.

Romijn's iodometric method was selected for use in the present research. Various precautions must be observed in its use before accurate results can be obtained. These precautions are given by Auerbach in the paper already mentioned[4].

H. and A. Euler[5] adopted the cryoscopic method for the analysis of their solutions, and later stated[6] that results of analysis performed by Romijn's method and the cryoscopic method agreed to within one per cent. To obtain such results their solutions must have been free from methyl alcohol, and - in order that they might have very little polymer - must either have been dilute or have been analysed very soon indeed after preparation. In the latter case/

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1) Z. anal. Chem., (1905), 44, 13.
2) Z. anal. Chem., (1897), 36, 18.
3) J. Amer. Chem. Soc., (1903), 25, 1028.
(Includes a bibliography).
4) Arb.a.d.Kais.Gesundheitsamte, (1905), 22, 584.
5) Ber., (1905), 38, 2551.
6) Ber., (1906), 39, 36.

case the solution, prepared from simple formaldehyde, (CH_2O), molecules, would not have had time to become transformed to any extent into polymer, in process of attaining equilibrium.

In this research, after analysis by Romijn's method the solutions were frequently analysed by the cryoscopic method 1). The results obtained in the latter analyses were always lower than those obtained by the first method. The second method is only of use for determining the molecular complexity of a formaldehyde solution. In performing an analysis with this end in view, it must be borne in mind that the equilibrium in a solution changes on dilution. The dilution necessary must therefore be done quickly, and the determination of the freezing point made as soon afterwards as possible.

As an example of the calculation involved in the two methods, the analyses figures for one of the formaldehyde solutions used, are given.

Romijn's Method:-

Two ccs. of the solution, 1) 135.3cc. N/10 Iodine.
weighing 2.056 gms. used up 2) 134.7cc. N/10 Iodine.
Average used up 135.0cc.

Now 1 cc. N/10 Iodine corresponds to .0015 gms. HCHO.
∴ 135 cc " " " " .2025 gms. HCHO.

i.e. .2025 gms. HCHO present in 2.056 gms. solution.

∴ 9.85 gms. HCHO per 100 gms. solution.

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1) Auerbach, Arb.a.d.Kais.Gesundheitsamte, (1905), 22, 584.

Cryoscopic Method:-

To 10 cc. of formaldehyde solution, weighing 10.28 gms., were added 10 cc. water, and the freezing point was determined.

Freezing point of solution = 4.904°.
Freezing point of water = 1.869°
$\therefore$ Lowering, Δ, = 3.035°C.

Number of gram molecules of HCHO per 1000 gms. H_2O is

$$\frac{\Delta}{1.86} = \frac{3.035}{1.86} = 1.632.$$

i.e. $1.632 \times 30 = 48.96$ gms. HCHO per 1000 gms. H_2O.
i.e. 48.96 gms. HCHO per 1049 gms. solution.

Now 10 cc. HCHO solution + 10 cc. H_2O together weighed 20.28 gms.

$\therefore$ Weight of HCHO per 20.28 gms. solution is

$$\frac{20.28}{1049} \times \frac{48.96}{1} \text{ gms.} \quad \text{i.e. } .9465 \text{ gms.}$$

But this weight of HCHO was present in the 10 cc. of the original solution. Therefore, the original solution contained .9465 gms. HCHO per 10.28 gms. solution.
i.e. 9.21 gms. HCHO per 100 gms. solution.

Method of performing the Experiments.

The method employed was, in outline, as follows: a solution of the base, at the chosen temperature, was rapidly mixed with a formaldehyde solution, at the same temperature, in such proportions that the result-ing solution/

solution was of a definite concentration with respect to both the base and the aldehyde. In some cases a sample was immediately withdrawn, with a pipette, for analysis; in others, a short interval elapsed between the time of mixing and the time of withdrawal of the first sample. The unused base was titrated with acid, phenolphthalein being used as indicator.

Temperature Limits:-

Most of the experiments were performed in a thermostat regulated to 50 ± .05°C. by a 300 cc. CCl_4 filled regulator, fitted to two Murray gas pressure regulators[1)] connected in parallel, air stirring being used. The experiments at 19.91°C. were carried out in a thermostat fitted with a paddle stirrer, and having a 600 cc. $CHCl_3$ regulator, connected with two Murray gas pressure regulators, and giving an accuracy of ± .01°C. (Only experiments at 50°C. included in thesis).

Apparatus used:-

The apparatus finally used is shown in outline in the sketch on the following page. The formaldehyde solution was placed in the boiling tube A, which was fitted with a syphon tube leading to the bottom of the similar tube B, and also with an inlet tube through which CO_2 - free air could be passed to force the liquid in A into the tube B. Each of the tubes was provided/

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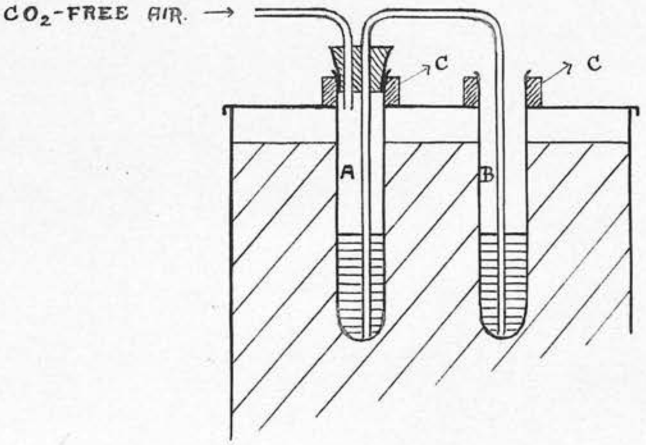
1) J. Chem. Soc., (1924), 125, 461.

provided with a heavy metal collar C, so that it would not float in the thermostat as the liquid was removed.



The solution of the base was placed in B, and while the apparatus was coming to the temperature of the thermostat, a plug of cotton wool in the mouth of the tube protected the base from more CO_2 than was contained in the air above the liquid. Experiment showed that this amount of CO_2 caused a negligible error.

After the formaldehyde solution had been forced into the tube B, and when the two solutions had been thoroughly mixed by the current of CO_2- free air, tube A was withdrawn from the thermostat, and tube B closed with an ordinary cork.

Method of Analysis:-

It was assumed that all the base which is used up goes to formate, and accordingly, to obtain a measure of the quantity of formate produced, one had only to measure the fall in concentration of the base. From the literature/

literature on the subject, and from a study of the reaction itself, this assumption seemed to be quite justifiable, within the limits of concentrations used. Accordingly, at a noted time from the time of mixing, a definite volume, usually 10 cc., was withdrawn with a pipette, the tube being freely opened for the purpose, but kept open for as short a time as possible. Experiment proved that errors caused by the introduction of CO_2 during these short periods when the tube was open could be neglected. The sample for analysis was at once poured into excess of cold distilled water to stop the reaction, phenolphthalein added, and the base remaining titrated with .02N HCl. Other indicators, such as methyl red, were used according to the nature of the base, but phenolphthalein was the most generally useful.

Possible Errors:-

A) Acidity of Formaldehyde Solution:-

The pure formaldehyde solutions prepared by steam distillation of the commercial 40% solution always showed an acid reaction to indicators. It was possible that the amount of base neutralised by this acid in one of the reaction velocity experiments might cause a considerable error, especially in those cases where the initial concentration of base was small. Experiments to test this point showed the error to be negligible. An example is as follows:-

5 cc. of HCHO solution/

5 cc. of HCHO solution, (approx. 16%), required .28 cc. of .02N. NaOH.

A simple calculation shows that a solution prepared from this HCHO and supposed to be .02N. with respect to the base, will, on account of the acidity in question, really be of the following concentrations:

HCHO.	Base.
8%	.0194N.
4%	.0197N.
2%	.0199N.

It will be found that the errors introduced here are well within the limits of experimental error, when it is shown how the velocity constant varies with the base concentration over the range commonly used in the experiments.

B) Carbonate Formation:-

When the base used was barium, strontium or calcium hydroxide, a precipitate of the insoluble carbonate was formed as the reaction proceeded. To find out whether this caused an appreciable error, the following experiments were performed.

1) Barium Hydroxide:- (.04N.)

60 cc. of a solution of barium hydroxide (.04N.) were placed in the thermostat at 50°C. Portions were withdrawn, in the same way as in the reaction velocity experiments, and were titrated with acid.

Time.	Vol. of .02N HCl required.
0 mins.	19.14 cc.
65 "	19.05 "
181 "	19.20 "
313 "	19.15 "
365 "	19.00 "

2) Barium Hydroxide:- (.02N.)

Procedure as above.

Time.	Vol of .02N HCl required.
0 mins.	9.35 cc.
44 "	9.27 "
79 "	9.37 "
153 "	9.31 "

These figures show that no appreciable error is introduced from this source.

C) Volatilisation of Formaldehyde:-

It might be objected that the practice of stirring up the mixture of base and aldehyde with a stream of CO_2- free air, previous to analysis, is not without its drawbacks. A proportion of the aldehyde might be volatilised in the process, and thus considerably alter the concentration of the solution. This objection is easily answered. Little air was blown through the mixture, and further, as has been shown by Auerbach 1) and recently by Blair and Ledbury 2) the partial vapour pressure of the dissolved formaldehyde is very small. It would be practically impossible to detect any change in the formaldehyde concentration due to this cause.

D) Change in Equilibrium of Formaldehyde Solution on Dilution by Base:-

It has previously been stated that the equilibrium in a formaldehyde/

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1) Arb.a.d.Kais.Gesundheitsamte, (1905), 22, 584.
2) J. Chem. Soc., (1925), 127, 26.

formaldehyde solution alters on dilution. This change takes a considerable time to complete, and it is just possible that a solution which analysed as 4% under certain conditions of equilibrium, might appear to be of another concentration when the equilibrium had changed. All experiments were performed in the same manner, only the time between the moments of mixing and the withdrawal of the first sample for analysis varying. Regular results, however, were obtained no matter how the experiments varied, so that this does not seem to be a serious source of error. In addition, at 50°C., equilibrium would soon be established again, and the error would appear as an "initial disturbance". No serious initial disturbance was noted. Standardisation of the formaldehyde solutions by reaction velocity, (See page 20), would estimate the united effects of concentration and molecular complexity of the aldehyde.

Attempt to apply Conductivity Methods to the Determination of the Velocity of Reaction.

Professor Walker 1) has determined the velocity of saponification of methyl acetate under the influence of caustic soda, by an application of the conductivity method. He found the method, even without special apparatus,/

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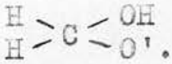
1) Proc. Roy. Soc., Series A, Vol. 78, 157; see also J. Chem. Soc., (1897), 71, 489.

apparatus, to be at least as accurate as the titration method carried out under specially favourable circumstances. It was thought that if this method could be applied to the present experiments increased accuracy might be obtained, and possibly also ease in execution.

The chief conditions for the convenient application of the method are, in his own words," first that there should be a considerable difference in conductivity between the initial and final systems, and second, that the change in conductivity should be proportional to the progress of the reaction". Are those requirements satisfied by the reaction under consideration? That the second condition is fulfilled can be shown as follows, where the action of caustic soda on formaldehyde is taken as an example.

At the beginning of the reaction the solution contains sodium and hydroxyl ions from the free caustic soda. There are, however, other ions present. As formaldehyde is a weak acid it forms a salt with the base, and this in turn is hydrolysed to a certain extent. The degree of hydrolysis is unknown owing to the uncertainty as regards the dissociation constant of formaldehyde as an acid, but on an average it may be taken as 50% hydrolysed when the concentration of formaldehyde is .67N. That part of the salt which is not hydrolysed is highly ionised, and thus there are in solution at the beginning of the reaction - in addition/

addition to the sodium and hydroxyl ions from the free caustic soda - sodium and complex methylene-glycol ions,  $\begin{matrix}H\\H\end{matrix}\!>C<\!\begin{matrix}OH\\O'\end{matrix}$. At the end of the reaction, provided there is an excess of formaldehyde, all the base will have been transformed, so there will be no hydroxyl ions, and no methylene-glycol ions. There will, however, be sodium and formate ions from the sodium formate produced. It is unlikely that the amount of methyl alcohol simultaneously formed will cause any appreciably difference in the conductivity, and accordingly it may be neglected.

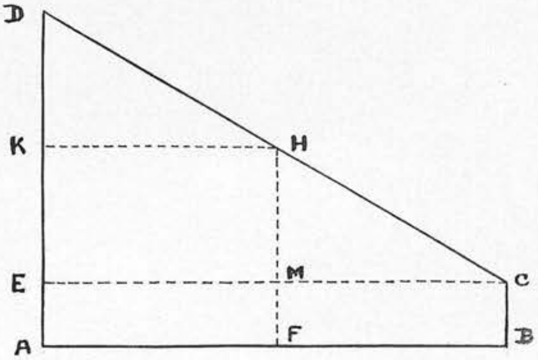
As far as the sodium ions are concerned, since the caustic soda, sodium formate and sodium salt of the formaldehyde are approximately equally ionised under the same conditions, the ionisation in dilute solution remains practically the same throughout the experiment. Accordingly the sodium ions need not be considered in connection with the change in conductivity.

Owing to the high velocity of the hydroxyl ions compared with those of the salt anions present, i.e. the formate and methylene-glycol ions, the initial conductivity is in large measure due to the former, and the fall due to their disappearance.

It now remains to show that the resultant fall in conductivity due to the~~ir~~ disappearance of hydroxyl and methylene-glycol ions, and to the appearance of formate ions is at every stage directly proportional to the progress/

progress of the reaction.

Supposing for the present that formaldehyde is not an acid, and that therefore no methylene-glycol ions are formed, a diagram such as the following can be drawn.



Let AD represent the initial conductivity due to the hydroxyl ions,

BC the final conductivity due to the formate ions alone,

AB will then represent the course of the reaction. In the diagram it does not include the time factor.

DC shows the fall in conductivity, not the rate of fall in conductivity.

It is only justifiable to join D and C by a straight line on the following assumptions:

1) That either no intermediate compound is formed between the aldehyde and the hydroxyl ions, or else that this compound, if formed, is always present in such quantity that its concentration bears a constant ratio to that of the hydroxyl ions. (Such a case will be discussed in a later paragraph. It has throughout/

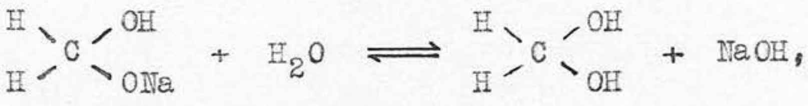
throughout this discussion been assumed that no unionised compound of the aldehyde and base is formed.)

2) That for every fall in concentration of hydroxyl ions, there is a simultaneous and corresponding rise in the concentration of formate ions, the concentration of the latter reaching a maximum value immediately on the disappearance of the base.

There seems to be no reason why both should not be assumed in the present case.

When the reaction has gone half way, i.e. at the point E, (= AB/2), it can be seen that the fall in conductivity (DK) is one half of the difference between the initial and final conductivities, i.e. one half of the total fall in conductivity (DE). The progress of the reaction is, therefore, proportional to the fall in conductivity.

Now take into consideration the acidic property of the formaldehyde. Part of the hydroxyl ions are replaced by methylene-glycol ions. The hydrolysis equation is



and accordingly

$$\frac{[CH_2(OH)_2][NaOH]}{[CH_2(OH)(ONa)]} = \frac{K_W}{k_a} = h.$$

When the formaldehyde is taken in excess, as is assumed/

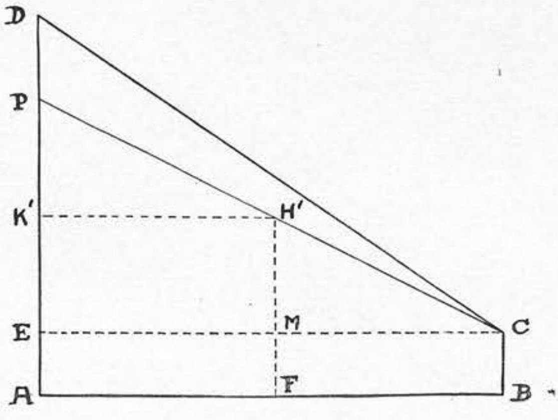
assumed here, the equilibrium takes the form

$$\frac{[NaOH]}{[CH_2(OH)(ONa)]} = \text{Constant.}$$

Owing to the approximately equal ionisation of the caustic soda, and the aldehyde salt, at the dilutions used

$$\frac{[OH']}{[H_2C(OH)O']} = \text{Constant.}$$

The concentration of methylene-glycol ions is, therefore, always a constant proportion of the concentration of hydroxyl ions, and accordingly the conductivity throughout will be a certain fraction of what the conductivity would have been had all the hydroxyl ions been free. In the previous diagram it is only necessary to choose a point P such that AP represents the initial conductivity of the solution when hydroxyl are partially replaced by methylene-glycol ions.



The previous proof that the reaction is proportional to the fall in conductivity can be applied here with the same result, and therefore the application of the conductivity method to the determination of the velocity of reaction in this case is at least valid, and the relationship a simple one.

Having settled that the method could with justification be applied to the reaction considered, a series of experiments were performed with various sizes and kinds of electrodes. The results were, however, extremely unsatisfactory. It was in every case found that a few millimetres change on the bridge wire was the best that could be obtained, while the corresponding drop in an acid titration of the base would be about 12 cc. There was thus no possibility of increasing the accuracy of the experiments by substituting conductivity for titrimetric analysis.

The reason suggested for the failure to obtain measurable differences of conductivity is that a large proportion of the hydroxyl ions had been replaced by slow-moving methylene-glycol ions. The number of these complex ions and their speed must have reduced the initial conductivity to a value not far removed from that due to the formate ions present at the end of the reaction.

Calculation of Results.

In most of the experiments such a large excess of formaldehyde was used that its concentration throughout an experiment could be taken as constant, and the only change to be considered was that of the base. Assuming the ordinarily accepted equation

$$2HCHO + NaOH = HCOONa + CH_3OH$$

the reaction/

reaction then reduces to one of the first order. The results have therefore in most cases been calculated from the formula

$$dx/dt \; = \; k.(a - x)$$

whence

$$k \; = \; 1/t.\log a/(a - x).$$

Constants have occasionally been obtained by the use of bimolecular or termolecular equations, but these were for the proof of some special point, and the formula employed is given.

a in the above formula was the concentration of base at the time chosen as t_0, measured by the volume of acid required in the titration. The various volumes of acid required at the subsequent times of analysis gave the values of $(a - x)$ for the different values of t. (Values were calculated, except when otherwise stated, using decadic logarithms.)

Accuracy of Results.

As a strict mathematical deduction of the accuracy of the results from the theory of errors, in the present case presented difficulties, an idea of the magnitude was obtained by comparing the results of experiments which should have given identical velocity constants. A few examples are given on the next page. Each pair of values consists of the average velocity constants obtained in two separate, but exactly similar experiments. The two values ought not to have differed.

	a)	b)	c)	d)
	338	344	334	340
	333	340	334	335
Difference.	5	4	0	5

	e)	f)	g)	h)
	342	377	309	314
	342	380	306	310
Difference.	0	3	309	313
			3	4

From these figures it is seen that, on the average, the error is not more than one per cent.

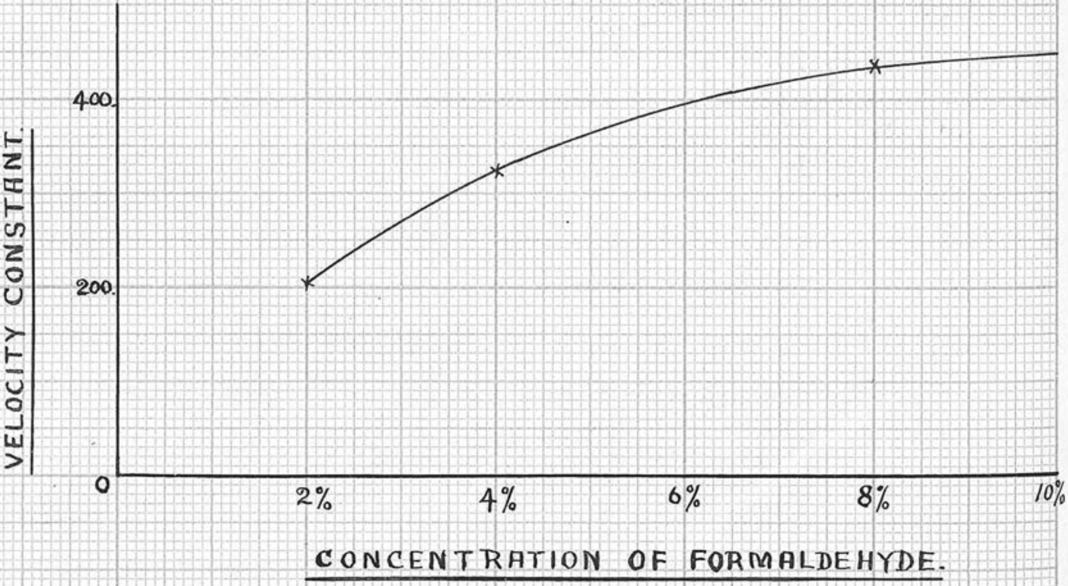
Standardisation of Formaldehyde Solutions by Reaction Velocity Methods.

Two solutions of formaldehyde were prepared as already described, and, on analysis by Romijn's Iodometric Method and the cryoscopic method, gave the following results.

Solution.	Romijn.	Cryoscopic.	% Polymer.
A.	9.85%	9.21%	9.75%
B.	15.06%	13.61%	14.40%

As would be expected, the cryoscopic method gave lower results than the iodine method, and the percentage of polymer increased with increasing concentration. This was proof that the results were comparatively accurate, and, accordingly, those solutions were employed for the determination of velocity constants with the bases, caustic soda and caustic potash.

The values of the velocity constant corresponding to the various concentrations of base and aldehyde were as follows. (Monomolecular - $k.10^5$)


VELOCITY CONSTANT.
400
200
0
2%
4%
6%
8%
10%
CONCENTRATION OF FORMALDEHYDE.

Solution A.

Conc. of HCHO.	Conc. of NaOH.			Conc. of KOH.
	.02N	.04N	.08N	.02N
2% (.67N)	205	199	207	202
4% (1.33N)	335	325	326	338
8% (2.67N)	442	433	438	433

Solution B.

Conc. of HCHO.	Conc. of KOH.	
	.04N	.08N
2.68% (.90N)	258	267
5.36% (1.80N)	383	393
10.72% (3.60N)	460	462

Since the values for the velocity constant, obtained with solution A were themselves regular, it was assumed that they were correct, and, using those values, a curve was drawn from which the concentration of a formaldehyde solution could be determined, when its velocity constant with a certain concentration of base, was known. In choosing values of the constants from which to plot the curve, it was assumed that these did not vary within the limits of base concentration used. Later work has justified this assumption. The mean values used were:-

HCHO 2% 203
HCHO 4% 334
HCHO 8% 437

Proof of the accuracy of the curve drawn was obtained when the values given by solution B were plotted. The points in each case lay either on, or very close, to the curve.

This then was evidently one way of determining the strength of a pure formaldehyde solution. Since the research/

research was expected to be in large measure a comparison of the velocity constants obtained with formaldehyde solutions under varying conditions as regards the bases, it was considered that the reaction velocity method was the best for estimating the strength of the aldehyde solution, as it would eliminate small errors due to the presence of traces of impurities which would not be recorded by the iodine method, but would influence the velocity of reaction. This method was accordingly adopted, and all solutions used in the following experiments were estimated, usually by determining their velocity of reaction with .04N sodium or potassium hydroxide, and approximately 4% formaldehyde. The concentration of the aldehyde solution was first found approximately by the iodine method.

THE ACTION OF SODIUM HYDROXIDE ON FORMALDEHYDE.

Loew[1] has shown that when formaldehyde and sodium hydroxide are mixed at higher temperatures sodium formate and methyl alcohol are produced. Delépine[2] has proved that the transformation takes place even at ordinary temperatures. Nef[3] also studied the reaction, and found the same two substances to be formed. It is, however, quite possible, by varying the conditions, to get other substances formed along with these mentioned. In the course of this research it was found that, at 50°C. a very low concentration of the base, say .001N, acting on a moderately concentrated (1N) formaldehyde solution, brought about some other transformation, resulting in the production of a yellow solution. (Calcium hydroxide was used in this experiment in order to reduce the time required, but there is reason to believe that sodium hydroxide would act in exactly the same manner.) Also, at the same temperature, when sodium hydroxide of 4N concentration, acted on a 4N formaldehyde solution a similar colouration was soon formed, the smell of aldehyde having disappeared.

It is thus evident that the concentration of the base and aldehyde, and, as has also been proved/

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[1] Ber. (1887), 20, 144; Ber. (1888), 21, 270.
[2] Bull. Soc. chim., (1897), 17, 939.
[3] Annalen, (1904), 335, 195.

proved, temperature, determine what reaction will take place. In neither of the cases mentioned, did the yellow solution smell of caramel. This suggests that the new reaction is not sugar formation. In one case, with strong solutions of caustic soda and aldehyde, a slight reduction of Benedict's solution was obtained, but the amount of sugar in no way corresponded with the intensity of the colour.

Loew[1] has made a generalisation in connection with formate and sugar formation. He says that, as a rule, the more concentrated the formaldehyde solution, and the stronger the base, the larger the quantity of formic acid produced, and consequently the smaller the quantity of sugar. Löb in his paper - " Zur Kenntnis der Zuckerspaltung, 1,"[2] refers to this point. He believes that the two reactions, sugar formation and methyl alcohol - formic acid production, take place quite independently of each other, and with different velocities. While at low temperatures and small alkali concentrations the first reaction is the more prominent, higher temperatures and alkali concentrations favour the second, apparently to such an extent that sugar formation and accompanying reactions are practically completely absent. If the temperature,and concentration of alkali are further raised, the optimum/

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1) Ber., (1889), 22, 471.
2) Biochem. Z., (1908), 12, 78.

optimum for the methyl alcohol - formic acid change is ~~past~~ passed, and sugar synthesis again becomes noticeable. Löb admits that the presence of sugar in his experiments could not be detected, but considers it probable that first of all sugar formation takes place, and that this sugar is extraordinarily quickly and completely decomposed to give the stable polyhydroxy acids found. It is doubtless these acids, - which Löb considers to be di- and tri- hydroxybutyric acids, - which caused the formation of the yellow colour, already mentioned in connection with the present research. It should be noticed that this colour only appears when the formaldehyde has been completely used up, and an excess of base remains. In a paper on the " Synthesis of Sugars from Formaldehyde," Ewart 1) supports the view that the nature of the products obtained depends chiefly on the concentration of the solutions and the temperature.

When the temperature is 50°C., the concentration of the formaldehyde .67N - 2.67N, and that of the base .02N - .08N, methyl alcohol and formic acid alone seem to be produced. Accordingly, these limits of concentration and the temperature 50°C., were chosen for the greater number of the experiments in this research. A few experiments were performed at other concentrations, but in none of these from which results are quoted/

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1) Proc.Roy.Soc.Victoria, 31,(N.S.),Pt.2, (1919), 379.

quoted was any other change noticed than the production of methyl alcohol and formic acid.

Although the literature already mentioned, and the general appearance of the experiments gave ground for belief in the equation

$$2HCHO + NaOH = HCOONa + CH_3OH$$

as representing the change completely, difficulty in the interpretation of the figures obtained made a closer study of the reaction a necessity.

Two different sets of analyses were performed. In the first set an attempt was made to estimate the formic acid and methyl alcohol produced, in the second, to determine the simultaneous fall in the concentration of the formaldehyde and sodium hydroxide.

Estimation of Formic Acid and Methyl Alcohol.

This method of analysis was not much used. The alcohol was estimated from the specific gravity of its aqueous solution, and by actual isolation and weighing. The formic acid was determined by oxidation with potassium permanganate 1). The results only gave a general idea that the main course of the reaction is as indicated by the equation

$$2HCHO + NaOH = HCOONa + CH_3OH$$

Second Method of Analysis.

The object of this estimation was to settle whether the ratio of the fall in concentration of the form-aldehyde/

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1) H.C.Jones, Amer.Chem.J.,(1895), 17, 539.

formaldehyde to that of the caustic soda had the value two, as was necessary if the accepted equation represents the resultant change which takes place.

The method of procedure was as follows. At a noted time a quantity of the solution was withdrawn and cooled in a flask immersed in ice water. At leisure, accurately measured portions were taken, and analysed, the sodium hydroxide being estimated by titration with acid, and the formaldehyde by Romijn's method.

Modifications of Romijn's Method necessary.

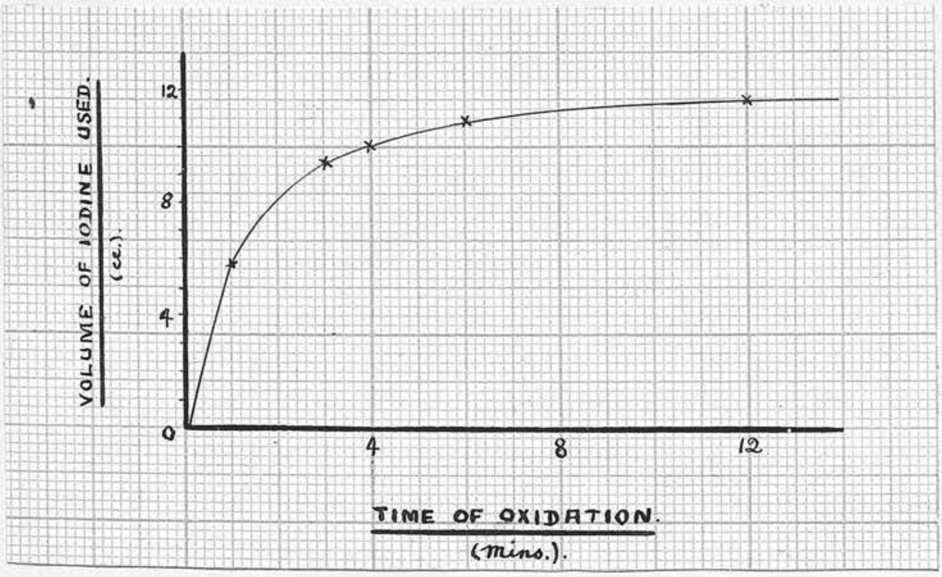
To be of value the measurements of fall in concentration of the base and aldehyde had to be accurate to at least one per cent. This precision was possible in the titration of the base with acid, but in the case of the formaldehyde, the solutions and methods used in its estimation under ordinary conditions were useless. To obtain an accurate value of the fall in concentration the solutions had to be .01N or less. The iodine taken was of this concentration, and the thiosulphate .005N,- both being accurately standardised.

For some time consistent results could not be obtained when these solutions were used with the very dilute formaldehyde employed. As an example, readings of from 6 to 12 cc. of .01N iodine were obtained when 12 cc. was the correct volume corresponding to the formaldehyde present.The cause of the trouble was found to lie in the time allowed for the alkaline hypoiodite solution/

solution to oxidise the aldehyde. Auerbach said that one minute appeared to be sufficient, and that acid could then be added and the unused iodine estimated. The following experiments were performed, the time during which the mixture remained alkaline and acid being varied.

Exper.	Time alkaline.	Time acid.	Vol. I_2 used.
1.	1 min.	3 mins.	5.9 cc.
2.	3 mins.	2 mins.	9.4 cc.
3.	3 mins.	6 mins.	9.6 cc.
4.	4 mins.	3 mins.	10.0 cc.
5.	6 mins.	3 mins.	11.0 cc.
6.	12 mins.	3 mins.	11.6 cc.

The following curve gives a better idea of the effect of the time of oxidation. The time of acidification may be neglected.



From the figures and curve it is seen that the time during which the formaldehyde solution should be left in contact with the alkaline oxidising agent is of great importance, whereas the time which elapses between acidification/

acidification and titration with the thiosulphate is of little consequence, as long as sufficient time be given for decomposition of the iodide, iodate and hypoiodite. In the experiment about to be described the time of oxidation was in all cases about twelve minutes, and the period of acidification three minutes. Consistent results were then obtained.

Experiment showed that the sodium formate and methyl alcohol,produced in the reaction, introduced no error through absorption of iodine.

Results of the Analysis:-

In the second column are given the volumes of iodine required in two separate determinations; the third gives the volumes of acid required to neutralise the unused alkali.

Time. (mins.)	Vol.I_2used. (cc.)	Vol.02N HCl. (cc.)	Conc.of HCHO.	Conc.of NaOH.
0	61.42:61.53	71.75	.614N	.287N
67	42.99:43.04	49.25	.429N	.197N
173	31.43:31.59	34.50	.314N	.138N
502	19.46:19.58	20.40	.194N	.082N
1587	11.41:11.61	10.57	.114N	.042N

Ratio, Mols. HCHO used / Mols. NaOH used:-

Between times.	Fall in conc. of HCHO.	Fall in conc. of NaOH.	Mols.HCHO. / Mols.NaOH.
0 & 67	.185N	.090N	2.06
0 & 173	.300N	.149N	2.01
0 & 502	.420N	.205N	2.05
0 & 1587	.500N	.245N	2.04
67 & 173	.115N	.059N	1.95
67 & 502	.235N	.115N	2.04
67 & 1587	.315N	.155N	2.03
173 & 502	.120N	.056N	2.14
173 & 1587	.200N	.096N	2.08
502 & 1587	.080N	.040N	2.00
		Average	2.04

These figures prove conclusively that for every molecule of sodium hydroxide used up, two molecules of formaldehyde are removed. This is the case at every stage of the reaction, and is not the resultant effect of several different changes proceeding at different rates, and therefore only true at the end of the reaction.

To sum up from the literature and analyses, it seems probable that at the concentrations used, form-aldehyde and sodium hydroxide react to give sodium formate and methyl alcohol as the only final products. Intermediate substances may be formed, and the course of the reaction may not be correctly represented by the equation

$$2HCHO + NaOH = HCOONa + CH_3OH$$

although this does give a true account of the final result of the change. Whatever be the stages in the reaction, they must be such that, during any interval, the amount of formaldehyde used up is twice the quantity of sodium hydroxide removed.

Course of the Reaction.

Assuming that the reaction consists in the production of methyl alcohol and sodium formate alone, or alternatively that, if there be another action, it takes place to such a small extent that its effect is negligible, - what is the course of the change? Does the reaction consist of a single termolecular process, or does/

does it take place in stages, each of lower order than the third? There are various methods by which the change might be supposed to take place. A few of these will now be given, and the evidence, in favour or otherwise, discussed.

1) First of all there is the method indicated in the ordinary equation

$$2HCHO + NaOH = HCOONa + CH_3OH$$

the reaction being of the third order.

2) The reaction might conceivably follow the course represented by the equations

$$HCHO + NaOH = HCOONa + 2H$$

$$HCHO + 2H = CH_3OH$$

Evidence in favour of this assumption is obtained in papers by Loew[1], and Nef[2] who found that sodium hydroxide and formaldehyde in presence of cuprous oxide, give sodium formate and liberate hydrogen. No methyl alcohol is formed, and this is ascribed to the catalytic action of the oxide causing the hydrogen atoms to become inactive by transformation into the molecular form. They are no longer able to reduce a molecule of formaldehyde, and so methyl alcohol is not formed.

The total change would be the result of two consecutive reactions, one bimolecular and the other termolecular. The observed order of the reaction would depend on the relative speeds of the two stages.

[1] Ber., (1887), 20, 144.
[2] Annalen, (1904), 335, 195.

3) There is good reason to believe[1] that in an aqueous solution of formaldehyde, by far the greater part of the unpolymerised aldehyde is present in the hydrated form, i.e. as methylene-glycol, $CH_2(OH)_2$. As it has two hydroxyl groups attached to the same carbon atom, the compound is unstable and cannot be isolated. This is, however, no reason for maintaining that it does not have any real existence; ammonium hydroxide is accepted as being present in an aqueous solution of ammonia.

It is possible that one molecule of simple formaldehyde might react with one molecule of the hydrated, methylene-glycol form, to give methyl alcohol and formic acid. The latter would be immediately neutralised by the base present.

$$\begin{aligned} HCHO + CH_2(OH)_2 &= HCOOH + CH_3OH \\ HCOOH + NaOH &= HCOONa + H_2O \end{aligned}$$

Assuming the second reaction to be instantaneous, the observed velocity would be that of the first change, and should obey a bimolecular equation.

4) The course of the reaction can be pictured in several different ways, each assuming the formation of sodium methyl peroxide. This is quite a stable compound, in aqueous solution, and acts as an oxidising agent of moderate power.[2] The methods are as follows.

(a)

$$\begin{aligned} HCHO + NaOH &= CH_3\text{-}O\text{-}O\text{-}Na \\ CH_3\text{-}O\text{-}O\text{-}Na + HOH &= CH_3OH + H\text{-}O\text{-}O\text{-}Na \\ H\text{-}O\text{-}O\text{-}Na + HCHO &= HCOONa + H_2O \end{aligned}$$

[1] Arb.a.d.Kais.Gesundheitsamte, (1905), <u>22</u>, 584.
[2] Ber., (1901), <u>34</u>, 738.

(b) $HCHO + NaOH = CH_3\text{-}O\text{-}O\text{-}Na$
$2CH_3\text{-}O\text{-}O\text{-}Na = CH_3OH + HCOONa + NaOH$

(c) $HCHO + NaOH = CH_3\text{-}O\text{-}O\text{-}Na$
$CH_3\text{-}O\text{-}O\text{-}Na + HCHO = CH_3OH + HCOONa$

In each case the reaction reduces to

$$2HCHO + NaOH = CH_3OH + HCOONa$$

They are accordingly valid interpretations of what happens in solution, as far as the fall in concentrations of the two reactants can show.

The first objection to this scheme is that a considerable amount of energy will be required for the production of sodium methyl peroxide. It must be admitted as unlikely that such a compound would be formed under the conditions of the experiments. However, supposing for the present, that a trace of the oxidising agent does result from the interaction of sodium hydroxide and formaldehyde, consider the above courses in turn.

(a) Sodium methyl peroxide is quite stable in presence of water, except in so far as it is the salt of a weak acid, and, therefore, undergoes considerable hydrolysis. It is rather unlikely that changes such as these shown would be necessary to bring about the oxidation. They are quite possible in presence of the reducing agent formaldehyde, but are not so probable as the other two methods.

(b) In these decompositions it is quite justifiable to consider the free acid, methyl hydrogen peroxide/

peroxide, as the active agent, instead of its sodium salt. Methyl hydrogen peroxide is an acid of strength comparable with that of phenol, and,consequently, its sodium salt will be largely hydrolysed in solution. Methyl hydrogen peroxide is not known to decompose spontaneously, as the equation suggests, but the corresponding ethyl hydrogen peroxide,[1] in presence of metallic silver as catalyst, decomposes to yield ethyl alcohol, acetaldehyde, and acetic acid. Silver oxide gradually dissolves in a dilute solution of ethyl hydrogen peroxide,probably as the acetate. These facts support the possible decomposition (b), in which case the base would play the part of the silver metal or oxide.

(c) If sodium methyl peroxide is formed as an intermediate step in the transformation, then this course of action is the most probable of the three. It seems reasonable to suppose that the oxidising agent would attack a molecule of formaldehyde directly, rather than proceed by some more or less devious path as indicated in (a) and (b). Of course, it is quite likely that the second step would take place in two stages,

$$CH_3\text{-}O\text{-}O\text{-}H + HCHO = HCOOH + CH_3OH$$
$$HCOOH + NaOH = HCOONa + H_2O$$

which, however, on account of the speed with which the neutralisation takes place, would reduce to a simple bimolecular reaction.

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[1] Ber., (1901), 34, 737.

As to the order of the reaction in these three cases, assuming no large excess of any reactant, (b) and (c) would each appear as two consecutive bimolecular reactions, while (a) would consist of three such. The apparent order of the whole change would depend on the relative speeds of each of the consecutive reactions.

Form of Equations used.

To obtain information which might enable a choice to be made between the possible courses, the experimental data were inserted in equations corresponding to the various cases. In the following tables, velocity constants are given in columns headed A to E. The formulae employed, and the equations to which they refer are as follows.

A. When a large excess of formaldehyde is present, its concentration does not change appreciably during an experiment, and the reaction

$$2HCHO + NaOH = HCOONa + CH_3OH$$

would thus appear as one of the first order. The figures in column A are the constants calculated from the monomolecular equation

$$dx/dt = k.(a - x)$$

whence

$$k = 1/t.\log a/(a-x)$$

In those cases where the aldehyde and base were present in more nearly equivalent proportions, it was, of course, impossible to obtain a monomolecular constant.

B. If the course of the reaction be as represented by the equations,

$$\begin{aligned} HCHO + CH_2(OH)_2 &= CH_3OH + HCOOH \\ HCOOH + NaOH &= HCOONa + H_2O \end{aligned}$$

and it be supposed that the second stage is infinitely fast, then the observed rate of reaction will be bimolecular, - neither reactant being in large excess.

In all the experiments the concentration measured was that of the sodium hydroxide. The quantity of formaldehyde which had disappeared was calculated from this, using the equation under examination. Accordingly in all the equations given x is taken as being the fall in concentration of the base. Since, in the above case, the concentration of the formaldehyde falls at twice the rate of that of the sodium hydroxide, the differential equation is:-

$$\begin{aligned} dx/dt &= k.(\text{Total conc.} HCHO - 2x)^2 \\ & k.(a - 2x)^2 \\ & 4k.(a/2 - x)^2 \end{aligned}$$

whence

$$k = x/4tb(b-x)$$

where $b = a/2$

C. If reaction 2, (page 31), occurs, i.e.

$$\begin{aligned} HCHO + NaOH &= HCOONa + 2H \\ HCHO + 2H &= CH_3OH \end{aligned}$$

and if it be assumed that the second stage takes place much more quickly than the first, then the apparent velocity of the reaction should be bimolecular. The differential equation takes the form,

$$dx/dt = k.(a - x)(b - 2x)$$

in which $\begin{cases} a = \text{total conc. of NaOH.} \\ b = \text{total conc. of HCHO.} \\ x = \text{fall in conc. of NaOH in time } t. \end{cases}$

The second term of the equation is (b-2x), as the effective concentration of the formaldehyde in the first stage of the reaction, i.e.

$$HCHO + NaOH = HCOONa + 2H$$

is the total concentration, and this falls twice as fast as does that of the caustic soda, although only one molecule takes part in this change.

This differential equation reduces to the form

$$dx/dt = 2k.(a-x)(c-x)$$

where $b = 2c$. On integration

$$k = \frac{1}{2(a-c)t} \cdot \log \frac{c(a-x)}{a(c-x)}$$

D. A series of constants have been calculated assuming that the apparent velocity of the reaction is proportional to the concentrations of the aldehyde and base, and that the fall in each is the same.

$$HCHO + NaOH = \text{etc.}$$

whence $$dx/dt = k.(a-x)(b-x)$$

and $$k = \frac{1}{(a-b)t} \cdot \log \frac{b(a-x)}{a(b-x)}$$

This is directly opposed to the experimental fact that the fall in concentration of the formaldehyde is at any time twice that of the sodium hydroxide. As, however, better constants are given by this equation than by some of the others, the values are included in the paper. What these figures mean is as yet unexplained.

E. According to the ordinarily accepted equation

$$2HCHO + NaOH = HCOONa + CH_3OH$$

the reaction/

reaction ought to be of the third order. The differential equation employed in these calculations is

$$dx/dt = k.(a-x)(b-2x)^2$$

where
$$\begin{cases} a = \text{total conc. of NaOH.} \\ b = \text{total conc. of HCHO.} \\ x = \text{fall in conc. of NaOH in time } t. \end{cases}$$

On integration

$$k = \frac{1}{\underline{4t}(a-c)^2}\left\{\frac{(a-c)x}{c(c-x)} + \log_e\frac{a(c-x)}{c(a-x)}\right\}$$

where $b = 2c$.

The reasons for using this formula, which is different from that usually employed, are given in a separate section at the end of this paper. (P. 132).

Tables of Constants.

Table 1 shows how the monomolecular velocity constant depends on the concentrations of formaldehyde and sodium hydroxide.

Table 2 gives the constants obtained when the concentration of base remains constant, and that of formaldehyde increases.

Table 3 indicates how the velocity constant varies with simultaneous increase in the concentrations of aldehyde and base.

Table 4 shows the variation of the monomolecular velocity constant with change in concentration of base, that of formaldehyde remaining unaltered.

All the experiments were performed at 50°C., and in the calculation of the constants decadic logarithms have been used, except/

except in evaluation from the termolecular formula,- page 38. As the volume of solution taken for each titration, and the normality of the acid used affect the magnitude of the constant in the bi- and termolecular formulae, these have all been calculated for a volume of 10 cc. and .02N acid.

Throughout the thesis, summaries only of the results have been given. The figures from which these have been calculated are collected at the end of the paper. (Page, 107).

TABLE 1.

Monomolecular velocity constants, (k.10^5).

Conc. of HCHO.	Conc. of NaOH. .02N	.04N	.08N
(.67N)	205	199	207
(1.33N)	335	325	336
(2.67N)	442	433	438

TABLE 2.

Values of $k.10^7$.

No.of Exper.	Conc. NaOH.	Conc. HCHO.	A.	B.	C.	D.	E.
(1)	.08N	.04N	-	109	22	22	2.9
				111	21	19	3.0
				114	20	17	3.2
				113	18	15	3.2
					19	13	4.3
(2)	.08N	.08N	-	85	35	33	2.4
				93	35	30	2.8
				91	31	25	2.9
				94	29	21	3.2
				100	27	17	3.6
				(106)	25	15	4.1
(3)	.08N	.16N	-	63	55	51	1.9
				58	50	42	2.1
				54	47	36	2.4
				50	44	31	2.6
				50	43	29	2.7
				47	41	26	3.0
				45	39	22	3.3
				44	38		4.4
				(41)	(36)		(5.8)
				(41)	(36)		(7.7)
(4)	.08N	.67N	21300	17	67	66	.48
			21300	17	68	67	.50
			20500	15	67	65	.50
			19800	13	66	63	.51
(5)	.08N	1.33N	34500	6.8	55	55	.20
			34400	6.3	55	55	.21
			33200	5.0	54	53	.21
			32100	4.3	53	52	.21
(6)	.08N	2.67N	44700	1.9	36	36	.067
			43600	1.5	36	35	.067
			43000	1.2	35	35	.067

TABLE 3.

Values of $k.10^7$.

No.of Exper.	Conc. NaOH.	Conc. HCHO.	B.	C.	D.	E.
(1)	.08N	.16N	63	126	51	1.9
			58	116	42	2.1
			54	108	36	2.4
			50	100	31	2.6
			50	100	29	2.7
			47	94	26	3.0
			45	90	22	3.3
			44	88		4.4
			(41)	(82)		(5.8)
			(41)	(82)		(7.7)
(2)	.16N	.32N	108	216	91	1.5
			104	208	86	1.5
			100	200	82	1.5
			97	194	78	1.5
			97	194	76	1.5
			95	190	74	1.5
			96	192	73	1.6
			78	156	(46)	(2.1)
(3)	.32N	.64N	138	276	112	1.0
			137	274	107	1.1
			132	264	99	1.1
			129	258	93	1.2
			125	250	87	1.2
			122	244	82	1.3
			120	240	80	1.3
(4)	.64N	1.28N	166	332	125	.76
			158	316	113	.81
			154	308	103	.89
			150	300	99	.90
			148	296	93	.97
			143	286	84	1.06
			138	276	78	1.09
(5)	1.28N	2.56N	168	336	121	.45
			161	322	104	.52
			154	308	89	.60
			152	304	79	.73
			147	294	70	.82
			145	290	64	.90

TABLE 4.

Conc. of HCHO.	Conc. of NaOH.	Monomolr. $k.10^5$
1.33N	.002N	396
	.005N	362
	.01N	336
	.02N	335
	.04N	325
	.08N	336
	.32N	476
.67N	.002N	270
	.005N	225
	.02N	205
	.04N	199
	.08N	207
	.20N	219

Graphs.

The figures in tables 2 and 3 are given in graphic form on page 44, these in table 4 on page 86.

Graph 1, giving the results of table 2, shows how the velocity constant varies when the concentration of base remains constant, and that of formaldehyde increases.

Graph 2, drawn from the data in table 3, indicates how the velocity constant varies with simultaneous increase in the concentrations of aldehyde and base.

As the figures in any one experiment in tables 2 and 3 show/

show a continuous rise or fall, values for drawing the curves were obtained by extrapolation to zero time. These data are given below.

TABLE 2.

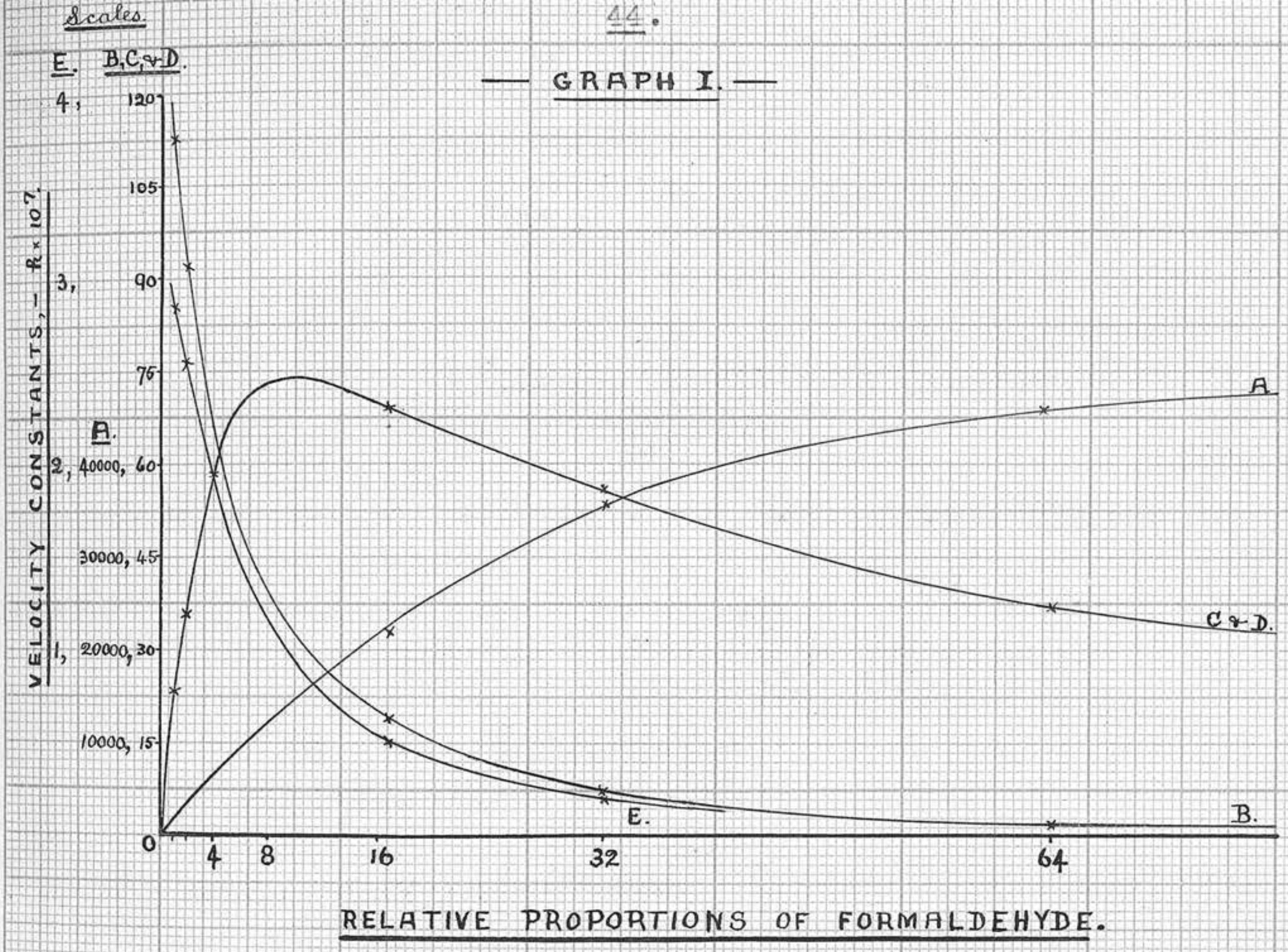
No. of Exper.	A.	B.	C.	D.	E.
1.		112	23.2	22.7	2.85
2.		92	36.0	39.0	2.55
3.		66	58.6	58.4	1.95
4.	22000	18.5	69.0	68.4	.50
5.	35500	7.2	56.5	56.1	.204
6.	46000	2.2	36.6	36.7	.067

TABLE 3.

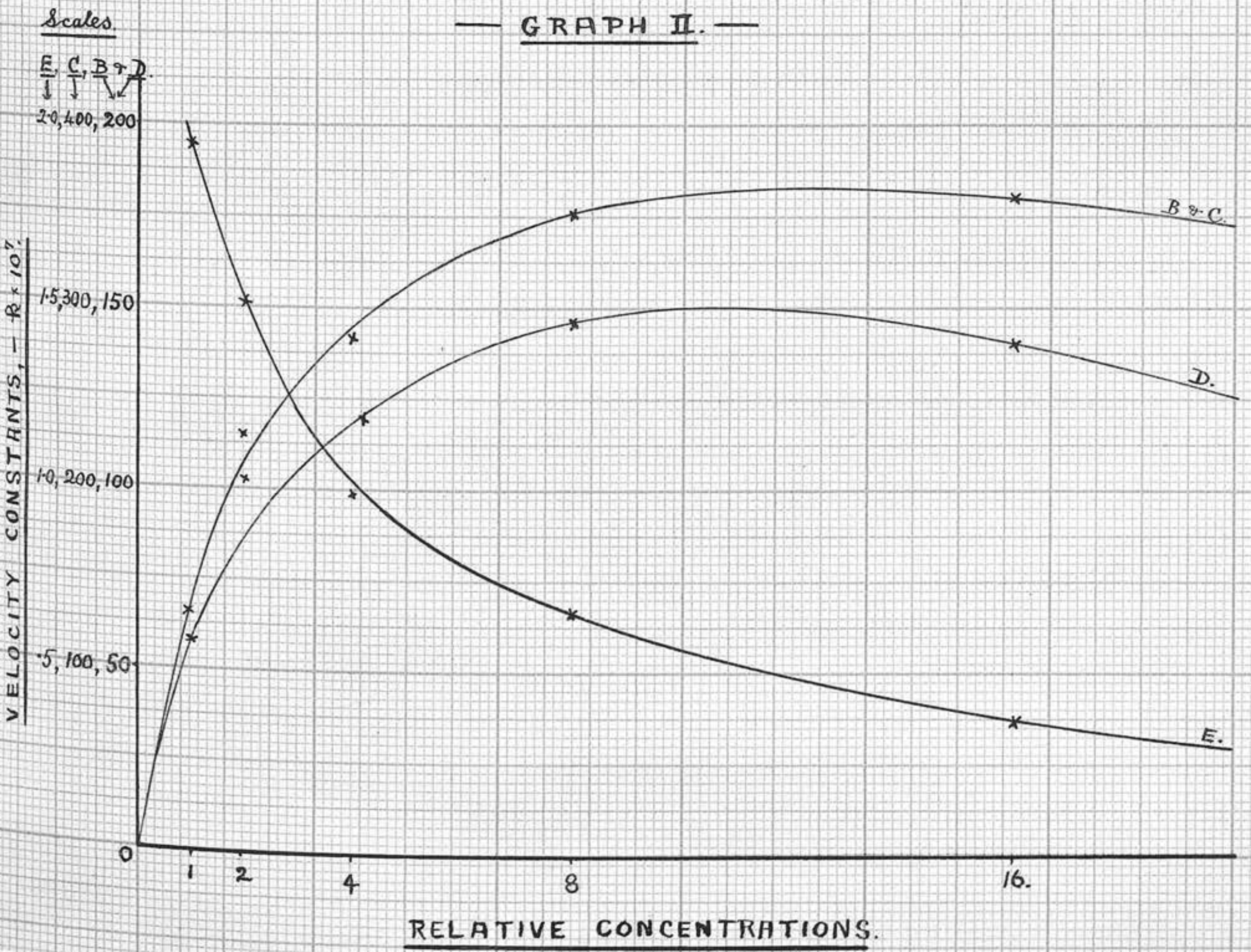
No. of Exper.	B.	C.	D.	E.
1.	66	132	58.4	1.95
2.	115	230	102	1.52
3.	142	284	119	.99
4.	175	350	146	.66
5.	180	360	140	.36

Very little information can, at the present stage, be drawn from these curves.

— GRAPH I. —



— GRAPH II. —



ORDER OF THE REACTION.

From the figures in tables 2, and 3, it would appear that the reaction follows no simple course. It is neither purely bimolecular nor termolecular. This is found in several ways. In the first place, when the experimental data are substituted in the expression for the particular type of reaction, a constant value for k is only occasionally obtained. The satisfactory constants in experiments 4, 5 and 6 of columns C, D and E of table 2, have little real significance, on account of the large excess of formaldehyde present.

In the second place, the velocity constant should be independent of the concentration of the reactants over wide ranges. The constants in tables 2 and 3 are marked by their dependence on this factor. Whether or not this variation in the value of k can be explained in a satisfactory manner, otherwise than by a complication of the reaction will now be considered.

Effect of Increase in Concentration of Reactants on the Velocity Constant.

The rate at which a substance A decomposes is, according to the mass action law, always proportional to its active mass, and, if this be taken as its concentration, measured in gram molecules per litre, then,

$$\text{Rate} = k.(\text{Conc. of A})$$

From this equation, it would be expected that if the concentration/

concentration of A were doubled, the rate of transformation would be doubled, - k remaining constant. In practice, however, it is frequently found that if the concentration of the reactant be doubled, - if the solutions be of moderate concentration, - k increases, which means that the rate has more than doubled.

This extra increase in the rate may be explained by taking into consideration a factor which is neglected in the deduction of the mass action law, i.e. the volume occupied by the dissolved molecules. The actual free space in which the reaction takes place is always less than the total volume of the solution. Taking the concentration of A as a gram molecules per litre, and supposing that the actual volume of the molecules of A per litre of solution is v_a, the free space in which the reaction may take place, is $(1-v_a)$ litres per litre of solution.

Now double the concentration of A, i.e. it becomes 2a gram molecules per litre. At the same time, the free space in which the particles move is decreased. It becomes $(1-v_{2a})$ litres per litre of solution, i.e. $(1-2v_a)$ litres per litre of solution,- assuming that the volume of a dissolved substance does not change on alteration of the amount of solvent present.

Assuming, - which is probably correct, - that, if the volume in which a reaction takes place is doubled, then the rate is halved, the rate is

1) proportional to the number of particles present.
2) inversely proportional to the free space.

In the two examples given, therefore, the rates should be

$$\text{Rate}_1 = k.a.\frac{1}{1-v_a} = \left\{k.\frac{1}{1-v_a}\right\}a = k_1 a$$

$$\text{Rate}_2 = k.2a.\frac{1}{1-2v_a} = \left\{k.\frac{1}{1-2v_a}\right\}2a = k_2 2a$$

where

$$k_1 = k.\frac{1}{1-v_a} \;;\; k_2 = k.\frac{1}{1-2v_a}$$

The constants $\underline{k}_{(1\,\&\,2)}$ are a function of the concentration, and increase with increasing concentration.

This represents the state of affairs frequently found in practice. When the concentration of the reactant is doubled, the second rate is more than twice the first, and the value of k increases.

If this be the explanation of the increase of the velocity constants in any series of experiments, involving a single reactant, then the following relation should hold.

$$\frac{k_1}{k_n} = \frac{k.1/(1-v_a)}{k.1/(1-nv_a)} = \frac{1-nv_a}{1-v_a}$$

When there are several reactants, the concentrations of both being increased in the same ratio each time, as for instance in the action

$$A + 2B = \text{etc.}$$

where $\underline{a}$ = conc. of $\underline{A}$; and $\underline{b}$ = conc. of $\underline{B}$.

$$\text{Rate}_1 = k.a.b^2.1/(1-v_1) = k_1 ab^2$$

$$\text{Rate}_n = k.(na)(nb)^2.1/(1-nv_1) = k_n(na)(nb)^2$$

$$\therefore \quad \frac{k_1}{k_n} = \frac{1-nv_1}{1-v_1}$$

When there are several reactants but the concentration of one only is varied, equations of the following type are obtained.

$$xA + yB = \text{etc.}$$

When the conc of A is a, and that of B is b, then

$$\text{Rate}_1 = k.(a^x.b^y).\ \frac{1}{1-v_a-v_b}$$

Suppose that the concentration of B is increased to nb,

$$\text{Rate}_n = k.(a^x.(nb)^y).\ \frac{1}{1-v_a-nv_b}$$

These may be written,

$$\text{Rate}_1 = k_1(a^x.b^y)$$

$$\text{Rate}_n = k_n(a^x.(nb)^y)$$

where

$$k_1 = k.1/(1-v_a-v_b)\ ;\quad k_n = k.1/(1-v_a-nv_b)$$

Therefore,

$$\frac{k_1}{k_n} = \frac{1-v_a-nv_b}{1-v_a-v_b}$$

i.e.

$$\frac{k_1}{k_n} = \frac{M-nv_b}{M-v_b} \qquad (\text{where } M = 1-v_a)$$

Application of these Principles to the Figures in Tables 2 and 3.

Table 2.

Only the constants in column A, and of experiments 1 - 4 in columns C and D need be considered. In the other cases the values of k decrease with increasing concentration of the reactants. The values of the velocity constants used in calculating the ratios were in all cases those obtained by graphic extrapolation for t = 0.

The ratios of constants are:-

Ratio.	A.	C.	D.
k_1/k_2	-	.64	.58
k_1/k_3	-	.40	.39
k_1/k_4	-	.34	.33
k_4/k_5	.62	-	-
k_4/k_6	.48	-	-

It has been proved that for the values in table 2, where the concentration of one reactant only varies,

$$\frac{k_1}{k_n} = \frac{M - nv_b}{M - v_b}$$

Where n is known, if the experimental value of the ratio k_1/k_n be accepted, a value of v_b can be obtained in terms of M. When this value of v_b is substituted in the equation, the ratio of velocity constants for some other value of n can be calculated. This ratio may be compared with the experimental value and thus a means is available of testing the applicability of the explanation proposed. Apply this to the figures in column A in the above table of ratios, and if $k_4/k_5 = .62$,

$$.62 = \frac{M-2v_4}{M-v_4}$$

$$v_4 = .275M$$

Therefore,

$$v_5 = 2 \times .275M = .55M$$

$$v_6 = 4 \times .275M = 1.10M$$

(The subscript figures, eg. v_4, here refer to the number of the experiment in table 2.)

The ratio k_4/k_6 can be calculated by making use of the value for v_6 thus obtained.

$$\frac{k_4}{k_6} = \frac{M - 4 \times .275M}{M - .275M} = - .138$$

The ratio k_4/k_6 obtained from the experimental values is, however, + .48, which proves that the explanation offered is inadequate to cover the facts.

The results obtained by applying this method of analysis to the first four experiments in columns C and D, of table 2, are given below. The ratio k_1/k_2 is employed to determine v_1.

Ratio.	Column C. Exper.	Column C. Calcd.	Column D. Exper.	Column D. Calcd.
k_1/k_2	.64	-	.58	-
k_1/k_3	.40	-.08	.39	-.26
k_1/k_4	.34	-4.41	.33	-5.31

No agreement is obtained even when other ratios are used to give a value for the volume. Once again, therefore, the explanation is seen to be insufficient.

Table 3.

Only columns B, C and D need be considered; the constants in column E show a continuous decrease. That the foregoing considerations are not the correct explanation of the variations observed is quite evident from a comparison of the calculated and experimental ratios of the constants.

Ratio.	Columns B & C. Exper.	Columns B & C. Calcd.	Column D. Exper.	Column D. Calcd.
k_1/k_2	.57	-	.57	-
k_1/k_3	.46	-.29	.49	-.29
k_1/k_4	.38	-2.00	.40	-2.00
k_1/k_5	.37	-5.43	.42	-5.43

It is, therefore, clear that allowance for the volume/

volume occupied by the molecules of the reactants is not sufficient to explain the irregularities in the constants, and thus make possible any settlement of the order of reaction. This doubtless plays its part, but it is not the only, and probably by no means the chief cause of the variations in the constants.

Number of Molecules of Sodium Hydroxide taking part in the Reaction.

As the methyl alcohol and sodium formate, produced in the reaction between sodium hydroxide and formaldehyde, affect the velocity of the change, the method about to be described has certain advantages for the determination of the number of molecules of sodium hydroxide taking part in the reaction, as values of the rate are employed which belong to the initial stages of the reaction when the products of the change have not accumulated. There are, however, dis-advantages associated with this method. The error in measuring small changes in concentration may be considerable, and, in the second place, the preliminary stages of the reaction may be liable to " initial disturbances". Consider the reaction

$$nA + n_1B = \text{etc.}$$

Perform two experiments with different concentrations of A, but the same concentration of B, and the following equations/

equations are obtained,

$$dC_1/dt = k.[A_1]^n[B]^n$$
$$dC_2/dt = k.[A_2]^n[B]^n$$

Divide the first by the second and take logarithms of both sides,

$$\log \frac{dC_1/dt}{dC_2/dt} = \log \frac{[A_1]^n}{[A_2]^n}$$

Therefore,

$$n = \frac{\log dC_1/dt - \log dC_2/dt}{\log [A_1] - \log [A_2]}$$

When applied to various experiments in which the concentration of formaldehyde was the constant term, the following values for the number of molecules of sodium hydroxide reacting were obtained.

Case 1:-	Exper.1.	Exper.2.
NaOH	.02N	.08N
HCHO	.67N	.67N

(The experimental data are to be found at the end of the paper, page 109).

To evaluate dC/dt a very small fall in concentration at the beginning of the experiment was divided by the short interval of time in which it took place. For the concentration of the reactant, the mean value of that at zero time and at the end of the interval mentioned, was taken.

$$dC_1/dt = 1.20/30 = .04 \ ; \quad dC_2/dt = 5.31/30 = .177$$
$$[A_1] = (9.2 + 8)/2 = 8.6 \ ; \quad [A_2] = (38.8 + 33.5)/2 = 36.14$$

Therefore,

$$n = \frac{\log .04 - \log .177}{\log 8.6 - \log 36.14}$$

$$= \underline{1.036}$$

The results of the various experiments are given in the table below.

Conc. of HCHO.	Conc. of NaOH.	n.
.67N	.02N	
"	.08N	1.036
1.33N	.02N	
"	.08N	1.031
2.67N	.02N	
"	.04N	.995
.67N	.02N	
"	.04N	1.018

In spite of the disturbing influences and errors to which this method of analysis is liable, the results leave little room for doubt as to the number of molecules of sodium hydroxide participating.

Further information as to the number of molecules participating in a reaction may be obtained in the following manner. The time taken to decompose a certain fraction of the original substance varies in the different orders. For the simple equations

$$k = \frac{1}{t}.\log\frac{a}{a-x}$$

$$k = \frac{1}{t}.\frac{x}{a(a-x)}$$

$$k = \frac{1}{2t}\left\{\frac{1}{(a-x)^2} - \frac{1}{a^2}\right\} \qquad \text{etc.}$$

where there is either only one substance present, or else all are initially present in equivalent quantities, it is readily shown that

$$t_{\varphi a} \propto \frac{1}{a^{n-1}}$$

where/

where $t_{\phi a}$ is the time required for the transformation of the same fractional part of the original substance, and n is the order of the reaction.

This function may be used for the determination of the order of the reaction, but in so employing it several assumptions are made. In the first place, k must be taken as independent of the concentration of the reacting substances during a given reaction, and, secondly, it is assumed that the reaction is in all cases affected by the same disturbing influences. A similar expression is obtained when two reactants are not initially present in equivalent quantities, but the one is always, at the beginning, a constant multiple of the other. The correct method of proving this would be to integrate an equation such as

$$dx/dt \quad = \quad k.(a-n_1x)^{n_1}(m_1a-n_2x)^{n_2}$$

and, in the integral obtained, to substitute $x = \phi a$. Such a procedure is difficult, and the desired end can be obtained by considering one or two simple cases.

For a bimolecular reaction, in which the original concentrations of the reactants are a and b,

$$k \quad = \quad \frac{1}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

If $b = ma$, then when $x = a/2$,

$$t_{\frac{1}{2}} \quad = \quad \frac{1}{a}.\frac{1}{k}\left\{-\frac{1}{m-1} \log \frac{m}{2m-1}\right\}$$

$$\text{i.e. } t_{\phi a} \propto \frac{1}{a^{n-1}}$$

Similarly, the integrated termolecular equation

$$k = \frac{1}{t}\cdot\frac{1}{(c-a)^2}\left\{\frac{x(c-a)}{a(a-x)} + \log\frac{c(a-x)}{a(c-x)}\right\}$$

when $c = ma$, and $x = a/2$, gives

$$t_{\frac{1}{2}} = \frac{1}{a^2}\cdot\frac{1}{k}\left\{\frac{1}{m-1} + \frac{1}{(m-1)^2}\log\frac{m}{2m-1}\right\}$$

i.e. $t_{\phi a} \propto \frac{1}{a^{n-1}}$

This can be continued for reactions of higher order, and in all cases it will be found that

$$t_{\phi a} \propto \frac{1}{a^{n-1}}$$

It should be noticed, that in the above examples b and c must either be taken in a known sufficiency, or else, instead of taking $x = a/2$, a much smaller fraction of a must be considered. If this were not done, the reaction would never reach the stage desired.

When k is assumed to be independent of the concentration, and the disturbing influences to be similar during the part of the reaction considered, the expression given above can be put into the form

$$\frac{t_{\phi a_1}}{t_{\phi a_2}} = \frac{a_2^{\,n-1}}{a_1^{\,n-1}}$$

whence,

$$n = 1 + \frac{\log t_{\phi a_1} - \log t_{\phi a_2}}{\log a_2 - \log a_1}$$

This expression will now be applied to the following experiments, on the assumption, that the value of the velocity constant when derived from the correct equation/

equation does not change with varying concentration of the reactants.

Exper.	Conc.NaOH.	Conc.HCHO.	$t_{\frac{1}{2}}$
1.	.08N	.16N	1130mins.
2.	.16N	.32N	325 "
3.	.32N	.64N	126 "
4.	.64N	1.28N	55 "
5.	1.28N	2.56N	28 "

When these values are substituted in the above equation, the following results are obtained.

From, 1 & 2	n = 2.80
1 & 3	2.58
1 & 4	2.45
1 & 5	2.33
2 & 3	2.37
2 & 4	2.28
2 & 5	2.18
3 & 4	2.20
3 & 5	2.09
4 & 5	1.97

This would seem to show that the reaction is, in low concentrations, termolecular, and at higher concentrations bimolecular. Evidence for and against this is obtained from a study of the constants given in tables 2 and 3. In table 3 the bimolecular constants in experiments 4 and 5 agree very well with each other, while those from lower concentrations show great variations in passing from one experiment to the other. An objection to this is, that at high concentrations, as in experiments 4 and 5, such good agreement between the constants of two experiments is hardly to be expected. An examination of table 2 shows that, in the first three experiments, bimolecular constants are very much dependent/

dependent on the concentration of the reactants, whereas those of the third order, in column E, have approximately the same mean value. This evidence appears to be somewhat misleading as, although the mean values of the first three experiments, in column E, are the same, yet the initial values, extrapolated for zero time, show a continuous fall with increasing concentration, and these initial values seem to be quite correct as they lie on a smooth curve, as is shown on page 44. The bimolecular constants mostly fall during a single experiment, whereas the ter-molecular values rise. This might be taken as indicating that the reaction takes place in several stages, - one part perhaps being termolecular and another bimolecular. The last three experiments in table 2 are useless for the purpose in hand, as, on account of the great excess of formaldehyde, their behaviour cannot be characteristic of a bi- or ter-molecular reaction.

The assumption that the reaction is, in low concentrations, termolecular can be tested in a way which will now be described. In the following table are given the times required for one fifth decom-position at the concentrations mentioned.

Exper.	Conc.NaOH.	Conc.HCHO.	$t_{1/5}$
1.	.08N	.04N	5000 mins.
2.	.08N	.08N	940 "
3.	.08N	.16N	250 "

If the reaction be supposed to conform to a particular order/

order, expressions can be obtained for each case giving the value of $t_{1/5}$. The ratios of these calculated times ought to agree with the values obtained from the figures in the above table, if the reaction really belongs to the order selected.

There is good reason for believing that if the reaction is termolecular, it proceeds according to the equation

$$2HCHO + NaOH = HCOONa + CH_3OH.$$

The equations for $t_{1/5}$ are then as follows.

(1) $\underline{HCHO} = .04N \quad (= b)$
$\underline{NaOH} = .08N \quad (= c)$

$$dx/dt = k.(b-2x)^2(c-x)$$
$$= 4k.(a-x)^2(c-x) \qquad \text{where } b = 2a.$$

Now $\underline{b} = .04N$, $\underline{c} = .08N$. Therefore $\underline{a} = c/4$, and

$$t = \frac{4}{9c^2k}\left\{\frac{3x}{(c/4-x)} + \log_e\frac{c-4x}{c-x}\right\}$$

When $x = c/5$,

$$t_{1/5} = \frac{4}{9c^2k}\left\{12 + \log_e 1/4\right\}$$

---

(2) $\underline{HCHO} = .08N \quad (= b)$
$\underline{NaOH} = .08N \quad (= c)$

$$dx/dt = k.(b-2x)^2(c-x)$$
$$= 4k.(a-x)^2(c-x) \qquad \text{where } b = 2a.$$

Now $\underline{b} = .08N$, $\underline{c} = .08N$. Therefore $\underline{a} = c/2$, and

$$t = \frac{1}{c^2k}\left\{\frac{x}{(c/2-x)} + \log\frac{c-2x}{c-x}\right\}.$$

When $x = c/5$,

$$t_{1/5} = \frac{1}{c^2k}\left\{2/3 + \log_e 3/4\right\}$$

---

(3) $\underline{HCHO} = .16N \quad (= b)$
$\underline{NaOH} = .08N \quad (= c)$

$$\begin{aligned} dx/dt &= k.(b-2x)^2(c-x) \\ &= 4k.(a-x)^2(c-x) \qquad \text{where } b = 2a. \end{aligned}$$

Now $\underline{b} = .16N$, $\underline{c} = .08N$. Therefore $\underline{a} = \underline{c}$, and

$$t = \frac{1}{8k}\left\{\frac{1}{(c-x)^2} - \frac{1}{c^2}\right\}$$

When $x = c/5$,

$$t_{1/5} = \frac{1}{c^2k} \cdot \frac{9}{128}.$$

The results obtained are given in the following table.

Experiments taken.	Ratios of $t_{1/5}$	
	Calculated.	Observed.
1 and 2	12.4	5.3
1 and 3	67.1	20.0
2 and 3	5.4	3.8

While the calculated and observed values rise and fall together, the agreement is not such as would prove the reaction to be a simple termolecular change.

Another method for investigating the mechanism of a reaction is to measure the velocity under conditions such that the concentration of only one of the reactants changes appreciably. The order of reaction, determined under these conditions, gives the number of molecules of the substance of variable concentration participating. In the reaction studied this leads to the conclusion that the reaction is monomolecular with respect to the sodium hydroxide. There is, however, some disturbing influence at work which/

which causes a slight but continuous fall in the constants in any one experiment. This is probably due to the production of a " negative catalyst," -possibly the methyl alcohol,- but the variation is not of such magnitude as to leave doubt as to the main order of reaction. It is very doubtful if this method could be applied to determine the number of molecules of formaldehyde reacting.

The evidence so far seems to prove that one molecule of sodium hydroxide takes part in the change, but, as to the complete reaction, it appears to be neither purely bimolecular nor termolecular. The disturbance might be caused by side, opposing or consecutive reactions, but the last seems to be the most probable.

It is frequently possible to elucidate the mechanism of a reaction from a study of the velocity constants obtained under varying conditions. An attempt will be made to do this in the present instance.

MECHANISM OF THE REACTION.

When lithium, sodium, potassium and tetramethylammonium hydroxides act on a large excess of formaldehyde the reaction which takes place gives satisfactory constants as one of the first order. The following table gives the average values of $k.10^5$ for the concentrations indicated. (Temperature 50°C.)

Base used.	Conc. of HCHO.	Conc. of base.		
		.02N	.04N	.08N
LiOH.	.67N	225	215	223
	1.33N	333	336	345
	2.67N	435	435	438
NaOH.	.67N	205	199	207
	1.33N	335	325	336
	2.67N	442	433	438
KOH.	.67N	202	204	207
	1.33N	338	334	342
	2.67N	433	436	437
$(CH_3)_4N.OH$.	.67N	203	205	206
	1.33N	334	333	339
	2.67N	424	421	430

As, owing to the constancy of the values of <u>k</u> in any one experiment, the reaction appears to be monomolecular with respect to the sodium hydroxide, when the formaldehyde is present in excess, the velocity constant would not be expected to vary with increasing base concentration, provided that the concentration of formaldehyde remained unaltered. This is found to be the case. An explanation is, however, required for the observed increase in the constants with increasing concentration of formaldehyde. When the concentration/

concentration of formaldehyde is doubled, the constant obtained is not twice its former value.

The differential equation for the interaction of these two substances may be written in general form as follows:

$$\text{Rate} = k.[HCHO]^{y}[NaOH]^{z}$$

As the reaction appears to be monomolecular with respect to the base, when the formaldehyde is in large excess, this may be written

$$\text{Rate} = K.[NaOH]$$

where $\underline{K} = k.[HCHO]^{y}$,- a practically constant term, as long as the concentration of formaldehyde is not altered. The variation of the velocity constant with increasing formaldehyde concentration might be explained by $\underline{y}$ being an integer other than unity. The value of $\underline{y}$ can be obtained from the relation

$$\frac{k.[HCHO]_1^{y}}{k.[HCHO]_2^{y}} = \frac{K_1}{K_2}$$

whence

$$y = \frac{\log K_1 - \log K_2}{\log [HCHO]_1 - \log [HCHO]_2}$$

Substituting the values given for sodium hydroxide in the table on page 61,

$\underline{y}$ (From 205 & 335) = .708
$\underline{y}$ (From 335 & 442) = .400

Apart from not approximating to a whole number other than unity, the values of $\underline{y}$ obtained do not even agree, and, accordingly, the variation in the constants cannot be explained in this simple way.

The difference/

The difference in the values of y might indicate that the total formaldehyde is not active, but that, as the total concentration increases, the " active " fraction decreases. Quite a number of explanations on similar lines can be advanced. The " active " formaldehyde might be simple (CH_2O), or polymeric $(CH_2O)_n$ molecules, hydrated simple or hydrated polymeric molecules: and again the actual substance taking part in the change might be some form of the sodium formaldehyde salt, i.e. unionised molecules of the salt or methylene-glycol ions. As regards the caustic soda, the concentration to be considered when the base actually takes part in the change, will not be the total concentration of the sodium hydroxide. The weak acid formaldehyde neutralises the base added, and it is only by the hydrolysis of the salt formed that any free sodium hydroxide is present. The concentrations of the ionised and unionised portions of this free base are the quantities to be considered.

It has up till the present been assumed that the reaction is monomolecular with respect to the sodium hydroxide. This is not necessarily the case. If it be supposed that the methylene-glycol ions are the " active " form which is being used up monomolecularly, then the hydroxyl ions will also be removed at a rate which gives a constant of the first order. This follows from the hydrolysis equation

$$CH_2(OH)(ONa) + H_2O \rightleftharpoons CH_2(OH)_2 + NaOH.$$

The salt and base are approximately equally ionised at the dilutions considered, and therefore

$$\frac{[OH']}{[CH_2(OH)O']} = \frac{h}{[CH_2(OH)_2]}$$

$$= \text{a constant for a given conc. of HCHO.}$$

The sodium hydroxide merely supplies the methylene-glycol ions, and does not enter into the main reaction, - the production of the formate ion and methyl alcohol.

Another possibility is that formic acid and methyl alcohol result from a true or pseudo- monomolecular reaction which does not involve the sodium hydroxide in any form. The acid produced neutralises the base, the disappearance of which gives a constant of the first order.

There are thus two possibilities since a monomolecular constant is obtained when the formaldehyde is present in large excess.

(1) The sodium hydroxide is taking part in the reaction monomolecularly, the other reactant or reactants,- some form or forms of formaldehyde,- being in great excess*, and so not entering into the equation.

(2) Some reactant, not sodium hydroxide, acts monomolecularly. The sodium hydroxide does not take part in the actual change, and is removed in some secondary way as indicated above. Any other reactants must be present in large excess.*

*(Any other reactants, not present in great excess, must be in equilibrium with some substance in large excess, so that their concentration will not change appreciably.)

Attempted Explanations of the Variation of the Constants based on different " active " Forms of Formaldehyde.

An endeavour was made to settle whether the formaldehyde entering into reaction required to be in some special form such as simple or polymeric molecules, either in the anhydrous or hydrated forms, or whether all forms were equally active. The experiment, which was performed with two pure formaldehyde solutions of different concentration, was as follows. A day or two after its preparation, the solution was analysed simultaneously by the iodometric, freezing point, and reaction velocity methods. The total amount of formaldehyde as estimated by Romijn's method would be expected not to vary, but polymerisation or depolymerisation might go on slowly for a considerable time, and this would be shown by the freezing point determinations. It was accordingly expected that a comparison of the freezing point and velocity of reaction figures would settle whether the simple, polymerised or total formaldehyde is the " active " form. This expectation was not realised, as the results of the experiments show.

SOLUTION 1.

Method.	Number of days after preparation.				
	3.	6.	13.	19.	55.
Romijn.	15.9%	15.86%	15.89%	15.86%	16.03%
Freezing Pt.	12.76%	12.86%	12.62%	12.71%	12.56%
Reaction Vel.	14.00%	14.15%	13.80%	13.70%	13.97%

SOLUTION 2.

	1.	3.	8.	33.
Romijn.	19.46%	19.49%	19.49%	19.46%
Freezing Pt.	16.28%	15.93%	15.93%	16.11%
Reaction Vel.	15.62%	15.35%	15.04%	15.62%

These figures show that the equilibrium in a formaldehyde solution does not alter after the first day. They might, however, be taken as indicating that the " active " form is not the total aldehyde, but a form which is present in smaller percentage the more concentrated the solution, i.e., as Auerbach 1) has shown, the simple molecules, anhydrous or hydrated. This is seen by comparing the iodine and reaction velocity figures in the two experiments.

Since the experiments were performed, reasons have appeared for believing that the change in equilibrium on dilution does not take very long to complete at 50°C., and would be reached in the early stages of an ordinary experiment. This means that these test experiments could not under any circumstances have given the desired information in the manner expected. However, it makes possible the application to the present research of values for the concentrations of simple and polymeric molecules, determined by Auerbach. 1) He considers that the equilibrium in a formaldehyde solution is essentially one between hydrated simple and trimeric molecules, and that, as regards the simple molecules at least, probably very few exist in the anhydrous form. Accepting his figures, there would be approximately the following concentrations of hydrated simple and trimeric molecules in the solutions used in this research.

1) Arb. a.d. kais. Gesundheitsamte, (1905), 22, 584.

Total HCHO.	Hydrated Simple.	Hydrated Trimeric.
.67N	.66N	.01N
1.33N	1.25N	.08N
2.67N	2.16N	.51N

(It is impossible to estimate the concentrations of anhydrous simple and trimeric molecules; it must be assumed, as has been done by Auerbach in his calculations, that all the formaldehyde is hydrated.)

An examination of these values leads to the conclusion that it is highly improbable that the hydrated trimeric molecules take any part whatever in the change. Their concentration is so variable that they could neither be the reactant which is being used up monomolecularly, nor yet could they possibly enter into the constant term, as being a reactant of which the concentration did not alter appreciably. This agrees with the suggestion already made on two occasions (pp.63 and 66) in support of simple molecules, as being the form in which the aldehyde takes part in the reaction. Taking everything into consideration, it would seem that simple molecules have more in their favour than polymeric molecules, but as to whether the simple molecules must be hydrated or not cannot be settled now.It is only the hydrated form which can be studied, and this by using the figures given by Auerbach. The points raised here will be tested later.

There is still another modification of the aldehyde in solution, - the sodium formaldehyde salt, produced according to the equation produced according to the equation

$$CH_2(OH)_2 + NaOH \rightleftharpoons CH_2(OH)(ONa) + H_2O$$

Being a salt this will be highly ionised, and the active form may be either the unionised molecules, or the methylene-glycol ions. It is necessary to determine the concentrations of these in the various solutions employed. Since it is the salt of a weak acid it is hydrolysed to a considerable extent, which can be calculated from the equilibrium

$$\frac{[CH_2(OH)_2]\ [NaOH]}{[CH_2(OH)(ONa)]} = h = \frac{K_w}{k_a}$$

The dissociation constant of water is approximately 6.5×10^{-14} at 50°C., but that of formaldehyde, acting as an acid, is only known at 0°C., and even then with no great certainty. The value given by Euler, and calculated from cryoscopic data, is 1.4×10^{-14}. From a study of the dissociation constants of glucose, fructose, saccharose, water, phenol and hydrocyanic acid at various temperatures, a probable value for formaldehyde at 50°C. is considered to be 13×10^{-14}. From these figures

$$h = \frac{K_w}{k_a} = \frac{6.5 \times 10^{-14}}{13 \times 10^{-14}} = \underline{.50}$$

The value of <u>h</u> having been obtained, the concentrations of unhydrolysed salt, free acid, and free base can be determined. For instance, in a solution originally .67N with respect to formaldehyde, and .04N as regards the sodium hydroxide, if $\underline{a}$ be the normality of the base/

base produced by hydrolysis,

$$\frac{(.67 - \overline{.04-a}).a}{(.04-a)} = h = .50$$

$$\underline{a = .0174N.}$$

Theoretically, it is only the concentrations of hydrated simple formaldehyde molecules which should enter into these equations. These concentrations are not known with accuracy, and, for the present, the total concentrations of formaldehyde have been used. This will be referred to again later. (page 79).

The following table gives, opposite the original quantities of formaldehyde and sodium hydroxide, the concentrations of free base, and of unhydrolysed salt.

Original HCHO.	Original NaOH.	Free NaOH.	Unhydrolysed Salt.
.67N	.02N	.0086N	.0114N
1.33N	.02N	.0055N	.0145N
2.67N	.02N	.0032N	.0168N

It is extremely difficult to obtain an accurate idea of the ionisation of the salt in a dilute solution such as this, and in presence of other electrolytes having an ion in common. This point will be discussed later, and, after suitable formulae have been developed, an attempt will be made to show whether or not any form of the salt is an active medium in the change. No reactant of which the concentration changes appreciably during an experiment can have its concentration included in the constant, and, since the reaction appears to be monomolecular, there/

there can only be one reactant present in variable quantity. As the formaldehyde salt is present in small and variable concentration, if it takes part in the reaction at all, it must be the reactant which is acting monomolecularly.

Different " active " Forms of Sodium Hydroxide.

As has been indicated previously, it is certain that the concentration of sodium hydroxide to be inserted in the equation is not simply the total concentration of base. Part of the hydroxide is present as aldehyde salt, and, while this keeps up a concentration of free base, which may be active, the salt itself cannot, for the purpose of determining the velocity of reaction, act as if it were an equivalent concentration of sodium hydroxide. It would act just as free base in titration with an acid stronger than formaldehyde, but it cannot take the place of free sodium hydroxide as the driving force in a chemical reaction. Accordingly, if the sodium hydroxide is an actual medium of change, the concentration to be used is that of free base, ionised or unionised.

Development of Equations.

Supposing for the present that the reaction takes place between formaldehyde and the total free sodium hydroxide, the general differential equation is

$$\text{Rate} = k.[\text{HCHO}]^y\,[\text{Free NaOH}]^z$$

If the/

If the formaldehyde be taken in great excess its concentration remains practically constant, and therefore $[HCHO]^y$ is a constant. The equation then becomes

$$\text{Rate} = \left\{k.[HCHO]^y\right\}[\text{Free NaOH}]^z$$

From the hydrolysis equation

$$\frac{[\text{Free NaOH}]}{[\text{Salt}]} = \frac{h}{[HCHO]}$$

Therefore

$$\frac{[\text{Free NaOH}]}{[\text{Salt}]+[\text{Free NaOH}]} = \frac{h}{[HCHO]+h}$$

i.e.

$$\frac{[\text{Free NaOH}]}{[\text{Total NaOH}]} = \frac{h}{[HCHO]+h} = c.$$

Therefore

$$[\text{Free NaOH}] = c.[\text{Total NaOH}]$$

for a given concentration of formaldehyde.

The original equation then becomes

$$\begin{aligned}\text{Rate} &= \left\{k.[HCHO]^y\right\}c^z[\text{Total NaOH}]^z\\ &\quad\left\{k.c^z[HCHO]^y\right\}[\text{Total NaOH}]^z\end{aligned}$$

Now the reaction is found to be monomolecular in presence of excess formaldehyde, and, therefore, if the free sodium hydroxide is the reactant, $\underline{z} = 1$, and the equation simplifies to

$$\text{Rate} = \left\{k.c.[HCHO]^y\right\}[\text{Total NaOH}]$$

Introducing the value of $\underline{c}$,

$$\text{Rate} = \left\{\frac{k.h}{[HCHO]+h}\cdot[HCHO]^y\right\}[\text{Total NaOH}]$$

This/

This holds for any concentration of formaldehyde. For a definite concentration of this, the constants will not vary with varying base concentration. They will, however, vary with change in that of the aldehyde.

But it will be either the hydroxyl ions, the sodium ions, or the unionised sodium hydroxide molecules which are the active agents. The above formula will then take the following forms.

Hydroxyl Ions active:-

If m be the fraction of the free sodium hydroxide which is ionised,

$$[OH'] = m.[\text{Free NaOH}]$$

Therefore

$$\begin{aligned} \text{Rate} &= \left\{k.[HCHO]^y\right\}[OH'] \\ & \left\{k.[HCHO]^y\right\}m.[\text{Free NaOH}] \\ & \left\{\frac{k.h.m.[HCHO]^y}{[HCHO]+h}\right\}[\text{Total NaOH}] \end{aligned}$$

For a definite concentration of formaldehyde, the constants will decrease with increasing base concentration. They will vary with change in concentration of formaldehyde on account of 1) varying HCHO
2) varying m.

Unionised Molecules of Sodium Hydroxide active:-

Where m is the fraction of the sodium hydroxide which is ionised, (1-m) is the part unionised, and, therefore,

$$[\text{Unionised NaOH}] = (1-m)[\text{Free NaOH}]$$

Therefore,

$$\text{Rate} = \left\{k.[HCHO]^y\right\}[\text{Unionised NaOH}]$$

Therefore

$$\text{Rate} = \left\{k.[HCHO]^{y}\right\}(1-m)[\text{Free NaOH}]$$
$$\left\{(1-m).k.[HCHO]^{y}\right\}[\text{Free NaOH}]$$
$$\left\{\frac{k.h.(1-m)[HCHO]^{y}}{[HCHO]+h}\right\}[\text{Total NaOH}]$$

The constants ought to rise slightly with increasing base concentration, that of formaldehyde being kept constant. They ought to vary with varying formaldehyde concentration for two reasons, 1) varying HCHO
2) varying m

Sodium Ions active:-

Assuming that no unionised complex containing the base is formed, - and this is practically certain,- the concentration of sodium ions remains nearly constant throughout an experiment. Accordingly, they need not be further considered here. There is reason to believe that they act catalytically, and this will be referred to later. (cf. pages 92 and 99).

Sodium Formaldehyde Salt active:-

It can be shown that similar formulae to the above, hold for the cases when the reaction is monomolecular with respect to the sodium formaldehyde salt, ionised and unionised.

(a) Methylene-glycol ions:-

Any other reactant must be present in large excess, and can therefore only be water or formaldehyde. A similar change has been shown to take place when paraformaldehyde is heated with 50% (vol) sulphuric

sulphuric acid[1], and thus formaldehyde is doubtless the only other reactant.

The equation is

$$\text{Rate} = \left\{k.[HCHO]^{y}\right\}[CH_2(OH)O']$$

$$\left\{\frac{k.m.[HCHO]^{y+1}}{[HCHO]+h}\right\}[\text{Total NaOH}]$$

(b) Unionised Salt Molecules:-

$$\text{Rate} = \left\{k.[HCHO]^{y}\right\}[CH_2(OH)(ONa)]$$

$$\left\{\frac{k.(1-m)[HCHO]^{y+1}}{[HCHO]+h}\right\}[\text{Total NaOH}]$$

Degree of Dissociation of Salt and Base:-

The great difficulty in the application of these formulae lies in deciding what is the degree of dissociation. It would not be difficult to assign a value to m were the salt or base alone. The trouble arises when an attempt is made to settle the apparent dissociation constant of the one in presence of the other. It is impossible to say exactly to what extent the sodium formaldehyde salt, and the free base, will be ionised. As the reaction proceeds sodium formate appears, and this has also to be taken into account. An application of the theory of isohydric solutions, based on the assumption that van't Hoff's dilution law /

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[1] Hammick and Boeree, J. Chem. Soc., (1922), 121,2738.
Dunlop, J. Chem. Soc., (1914), 105,1155.

law holds for these strong electrolytes, leads to the conclusion that the degree of ionisation of the aldehyde salt and free base will both be diminished. Experiment has, however, on more than one occasion shown an increase when the theory predicted the opposite. In addition to the uncertainty thus introduced, there are other sources of error which make it quite useless to calculate the concentration of the unionised salt and base. The degrees of ionisation of the sodium hydroxide and aldehyde salt are not known with accuracy, especially after calculation to 50°C., they are large and do not vary much over the range of concentrations used. Accordingly, any error in these is magnified greatly in the calculation of the small concentration of unionised substance. Moreover, the concentrations of the salt and base, on which the whole calculation rests, are deduced from the hydrolysis equation and therefore depend on the value of <u>h</u> which may vary considerably from the correct figure, owing to the uncertainty of the dissociation constant of formaldehyde at 50°C. Further, the concentration of formaldehyde to be substituted in the hydrolysis equation should be that of hydrated simple molecules, and nothing really definite is known of this.

This criticism applies only in part to the concentrations of total and ionised salt and free base. Their total concentrations are uncertain to an extent, but accepting these as the most probable figures, the calculated/

calculated concentrations of hydroxyl and methylene-glycol ions cannot be very far from the correct values.

The following table gives the figures obtained by the application of van't Hoff's formula to the free sodium hydroxide, on the assumption that the degree of ionisation of the salts present is not greatly affected by the presence of the sodium ions from the base. The base itself gives a constant with this dilution formula. The concentrations of unionised sodium hydroxide, although liable to serious error, are included to give an idea of the various magnitudes.

Table of Concentrations.

A = Number of experiment.
B = Concentration of formaldehyde.
C = Concentration of sodium hydroxide, -from qty. added.
D = Concentration of free sodium hydroxide,-hydrolysis.
E = Concentration of formaldehyde salt.
F = Degree of ionisation of free sodium hydroxide.
G = Average ionisation of salts and base present.
H = Concentration of hydroxyl ions, from free base,-neglecting influence of salts.
I - Concentration of unionised free base,-neglecting influence of salts.
J = Fall in conc. of OH', and rise in conc. of undiss. free base, due to influence of salts, and calcd. from van't Hoff's dilution law.
K = Conc. of OH',-allowing for total conc. $Na^{\cdot}$.
L = Conc. undiss. free base,- allowing for total $[Na^{\cdot}]$.

A.	1.	2.	3.	4.	5.
B.	.67N	.67N	.67N	1.33N	2.67N
C.	.02N	.04N	.08N	.02N	.02N
D.	.0086N	.0174N	.0355N	.0055N	.00318N
E.	.0114N	.0226N	.0445N	.0145N	.01682N
F.	.966	.952	.933	.972	.979
G.	.94	.92	.91	.94	.93
H.	.00831N	.0166N	.0331N	.00535N	.00311N
I.	.000292N	.00084N	.00238N	.000153N	.000067N
J.	.000235N	.000643N	.00175N	.000227N	.000178N
K.	.00807N	.0159N	.0314N	.00512N	.00293N
L.	.000527N	.00148N	.00413N	.00038N	.000245N

Application of Formulae Derived.

Hydroxyl Ions active.

The formula derived on the assumption that the hydroxyl ions from the free base are the only part of the sodium hydroxide that enters into the reaction, will now be applied to the figures of experiments 1, 4 and 5 , page 76. For m the following ratio will be used,

$$m = \frac{[OH']}{[\text{Total free NaOH}]} \quad \text{- allowing for excess Na}^{\cdot}$$

The degree of ionisation of the sodium hydroxide does not remain constant during an experiment, but this does not invalidate the proposed calculation. The variation will not be considerable, and, moreover, the figures used are comparable as they are all calculated for the concentrations present at the beginning of an experiment. There is no doubt as to the values of K to be chosen, - they are constant within any experiment. The formula may be written,

$$\text{Rate} = K.[\text{Total NaOH}]$$

where,

$$K = \left\{ \frac{k.h.m.[HCHO]^y}{[HCHO]+h} \right\}$$

For two different concentrations of formaldehyde, but the same concentration of sodium hydroxide, this can be put in the form:-

$$y = \frac{\log K_1 - \log K_2 + \log\{m_2([HCHO_1]+h)\} - \log\{m_1([HCHO_2]+h)\}}{\log[HCHO_1] - \log[HCHO_2]}$$

When/

When the concentrations of total formaldehyde, (p.67), are substituted in the equation , and K_1 and K_2 have the values

(205 and 335) $y = 1.37$
(335 and 442) $y = 1.21$

If the concentrations of hydrated simple formaldehyde molecules be used, then when K_1 and K_2 have the values

(205 and 335) $y = 1.43$
(335 and 442) $y = 1.29$

These results show that the reaction does not take place between hydroxyl ions and formaldehyde, either as hydrated simple molecules, or, acting as a whole. The value of y must be an integer, and it would require a considerable variation in the quantities concerned to make it such. The use of the total concentration of formaldehyde is justifiable as we have no proof that the concentrations of hydrated simple molecules are correct, and also several forms of formaldehyde may be equally active in the reaction with the hydroxyl ions.

Unionised Sodium Hydroxide Molecules:-

Owing to the relatively large error to which the concentrations of unionised sodium hydroxide molecules are liable, it is useless to carry out any calculations involving them. If this is the form in which the base acts, then the constants ought to rise slightly with increasing base concentration. There is reason to believe that they do increase steadily, and this point/

point will be considered later.

Methylene-glycol Ions:-

If the values of m occurring in the above example be compared, they will be found to vary very little indeed, and, if they be omitted from the equation, the results obtained do not differ appreciably from these already given. Accordingly, to get an idea of the value of y, the variation in m may be neglected, and it will cancel out, as k was found to do, (p.77). This observation, based on values obtained by substituting the total concentration of formaldehyde in the hydrolysis equation, (p.69), shows that it is useless to attempt to obtain increased accuracy by using the concentrations of hydrated simple molecules in that equation. The values of (1-m) thus derived, would even then be too uncertain for use, and, as has been shown, the value of m has too little effect to make the calculation, which would at best be doubtful, worth while.

Apply this to the sodium formaldehyde salt, and, as the presence of the sodium ions from the free base does not affect its ionisation to any extent, and as this does not vary much over the range of concentrations considered, m may here also be cancelled out. The equation,

$$\text{Rate} = \left\{ \frac{k.m.[HCHO]^{y+1}}{[HCHO] + h} \right\} [\text{Total NaOH}]$$

thus gives, /

thus gives,

$$\frac{[HCHO_1]^{y+1} \times ([HCHO_2] + h)}{([HCHO_1] + h) \times [HCHO_2]^{y+1}} = \frac{K_1}{K_2}$$

whence,

$$y = \frac{\log K_1 - \log K_2 + \log([HCHO_1] + h) - \log([HCHO_2] + h)}{\log[HCHO_1] - \log[HCHO_2]} - 1.$$

When the concentrations of total formaldehyde are substituted in the equation, and K_1 and K_2 have the values

(205 and 335) $y = .35$
(335 and 442) $y = .19$

If the concentrations of hydrated simple formaldehyde molecules be used, then when K_1 and K_2 have the values

(205 and 335) $y = .41$
(335 and 442) $y = .27$

It is therefore evident that it is not the methylene-glycol ions that are acting monomolecularly.

Unionised Formaldehyde Salt Molecules:-

What was said with regard to the concentration of unionised sodium hydroxide molecules holds for these also. They will, therefore, not be considered further, except to point out that if this is the form in which either the base or aldehyde act monomolecularly, then the constants ought to rise slightly with increasing base concentration. As has already been indicated, there is reason to believe that they do so.

It would thus appear that no simple explanation is to be found along the lines studied, unless it be that/

that either the unionised molecules of the base or aldehyde salt are the key to the problem. More information on this point may be obtained when the experiments with other bases are considered. Another suggestion is that a wrong value has been chosen for the hydrolysis constant h, but calculation shows that this cannot be the reason. The fact that the sodium formate and methyl alcohol produced are positive and negative catalysts, respectively, for the reaction, offers no explanation of the variation of constants from one experiment to another. Some light may be thrown on the mechanism of the reaction by a study of the constants obtained with other bases. Barium, strontium and calcium hydroxides will be considered first.

Barium, Strontium, and Calcium Hydroxides.

In the case of barium, strontium, and calcium hydroxides it is found that the constants increase both with increase in concentration of aldehyde and of base. The constants obtained are as follows.

Base.	Conc. HCHO	Constants. Conc. of Base.			Max.Deviations. Conc. of Base.		
		.02N	.04N	.08N	.02N	.04N	.08N
$Ba(OH)_2$	.67N	232	245	290	17	27	48
	1.33N	367	383	420	24	20	54
	2.67N	460	479	517	29	21	29
$Sr(OH)_2$	.67N	248	272	307	29	19	78
	1.33N	392	393	450	23	19	80
	2.67N	470	494	544	5	16	24
$Ca(OH)_2$	.67N	288	-	-	35	-	-
	1.33N	440	-	-	25	-	-
	2.67N	563	-	-	34	-	-

The question arises,- is the reaction really monomolecular with these bases? In the second table above are given the maximum deviations in the constants in each experiment. While they are not regular, they show quite clearly that, as the ratio of base to formaldehyde increases, the deviation from a mono-molecular constant becomes more marked. With the exception of these cases where the deviations are over 48, the reaction may be considered monomolecular. In the other cases the concentration of aldehyde has become insufficiently great to keep the reaction apparently monomolecular. This would suggest that the base plays some direct part in the change, and does not, as was previously suggested, only keep up a con-centration of methylene-glycol ions, or neutralise acid produced.

It is interesting to note that there is regularity in the increase of the constants.

		$Ba(OH)_2$					$Sr(OH)_2$		
	13		45			24		35	
135		138		130	144		144		143
	16		37			24	(416)	34	
93		96		97	78		78		78
	19		38			24		34	(528)

In drawing up the table for strontium hydroxide, <u>416</u> has been substituted for <u>393</u> and <u>528</u> for <u>544</u>. This seems quite justifiable from the regularity thus produced. Thus/

Thus a certain increase in concentration of the base produces a definite increase in the constant, irrespective of the concentration of formaldehyde, and, similarly, a certain increase in concentration of formaldehyde produces a definite increase in the constant, irrespective of the concentration of base.

It is possible, in a general way, to say that the increase in constants with increasing concentration of formaldehyde - that of base remaining unchanged - is merely due to this formaldehyde which is present in large excess, not changing appreciably in concentration during an experiment, and thus making the reaction appear as of lower order, but characterised by a higher constant, - dependent on the concentration of formaldehyde. A correct explanation on these lines is, as has been shown, very difficult. Leaving this, however, for the present, how is the increase in the velocity constants with increasing concentration of base to be explained?

That the bases under examination do not differ radically in their mode of action from those already considered, is proved by a comparison of the conductivities of sodium hydroxide and barium hydroxide alone, and when mixed with formaldehyde, - it being assumed that the course of the reaction is the same at 25°C., as at 50°C. The conductivity figures are given in the table on the following page.

Conductivities at 25°C.

Conc. of base.	Conc. of HCHO.	Conductivities.	
		NaOH.	$Ba(OH)_2$
.1N	-	2.18×10^{-2}	2.03×10^{-2}
.05N	-	1.14×10^{-2}	1.08×10^{-2}
.025N	-	5.87×10^{-3}	5.73×10^{-3}
.1N	.1N	1.77×10^{-2}	1.65×10^{-2}
.05N	.05N	9.95×10^{-3}	9.48×10^{-3}
.025N	.025N	5.40×10^{-3}	5.24×10^{-3}
.1N	.5N	1.11×10^{-2}	1.05×10^{-2}
.05N	.5N	5.66×10^{-3}	5.52×10^{-3}
.025N	.5N	2.93×10^{-3}	2.92×10^{-3}

The results, in every case, run closely parallel. Had there been any essential difference in the mode of action, it is almost certain that this would have been shown up in the conductivity measurements. Had, for instance, an unionised complex been formed by the barium hydroxide and formaldehyde, the reduction in conductivity thus produced would, most probably, at all the dilutions considered, not have agreed so closely with that of the sodium hydroxide and formaldehyde, supposing the reduction in this case to be due to mere neutralisation, with consequent replacement of hydroxyl by slow-moving methylene-glycol ions. It is practically certain then, that, whatever be the cause of the reduction in conductivity, it is due to the same effect in both cases.

Further proof that the reaction is essentially the same with the alkalies and alkaline earths, -and with tetramethylammonium hydroxide - is obtained when curves are plotted showing how the velocity constant varies/

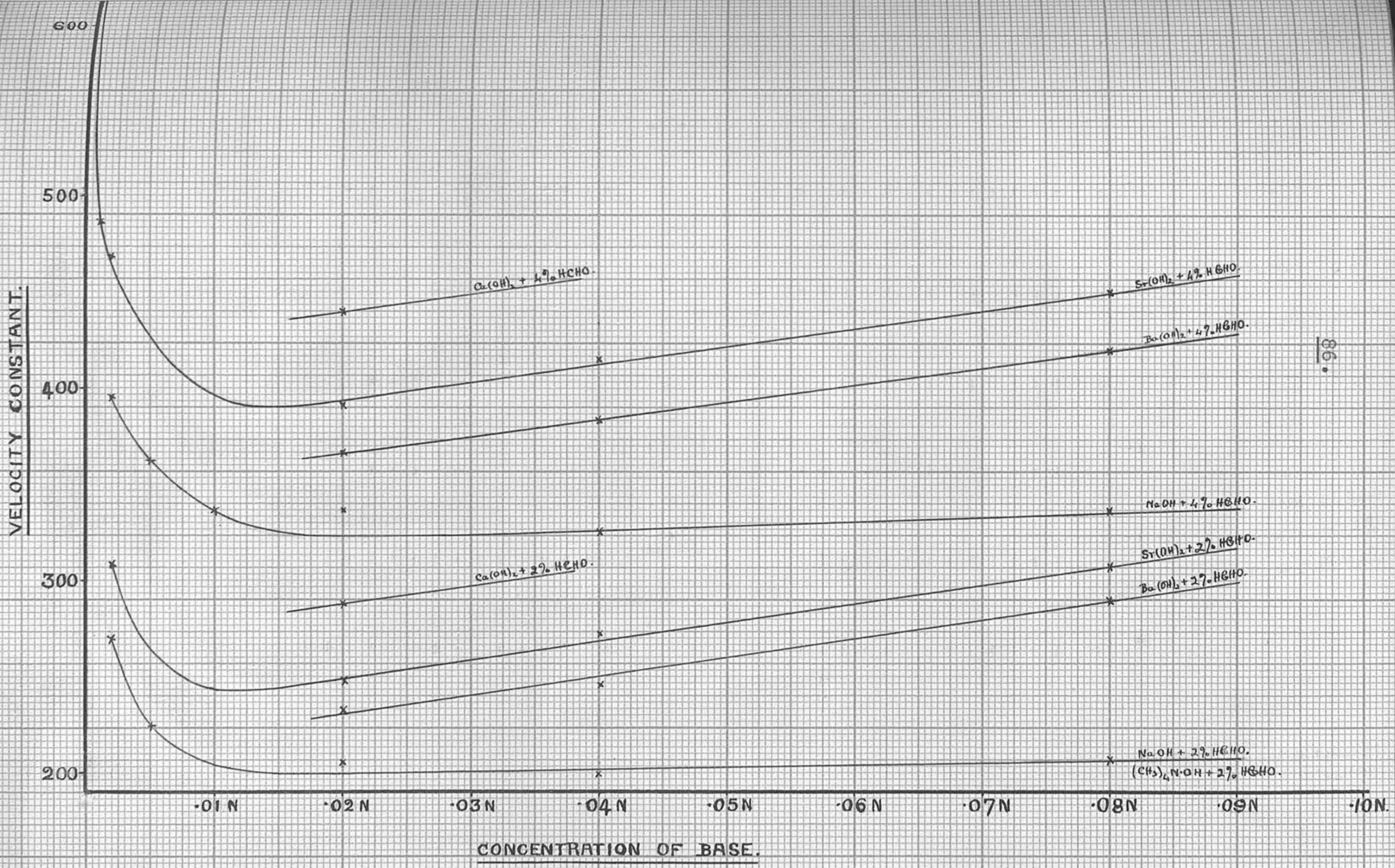
(Monomolecular, - $k \times 10^5$)

varies with change in concentration of the base.

Data for curves.

Base.	Conc. HCHO.	Conc. of Base.				
		.0005N	.001N	.002N	.005N	.01N
NaOH	.67N	-	-	270	225	-
	1.33N	-	-	396	362	336
	2.67N	-	-	-	-	-
$Ba(OH)_2$	.67N	-	-	-	-	-
	1.33N	-	-	-	-	-
	2.67N	-	-	-	-	-
$Sr(OH)_2$	.67N	-	-	309	-	-
	1.33N	863	486	467	-	-
	2.67N	-	-	-	-	-
$Ca(OH)_2$	.67N	-	-	-	-	-
	1.33N	-	-	-	-	-
	2.67N	-	-	-	-	-
$(CH_3)_4N.OH$	.67N	-	-	255	-	-
	1.33N	-	-	-	-	-
	2.67N	-	-	-	-	-

Base.	Conc. HCHO.	Conc. of Base.				
		.02N	.04N	.08N	.2N	.32N
NaOH	.67N	205	199	207	219	-
	1.33N	335	325	336	-	476
	2.67N	442	433	438	-	-
$Ba(OH)_2$	.67N	232	245	290	-	-
	1.33N	367	383	420	-	-
	2.67N	460	479	517	-	-
$Sr(OH)_2$	.67N	248	272	307	-	-
	1.33N	392	416	450	-	-
	2.67N	470	494	528	-	-
$Ca(OH)_2$	.67N	288	-	-	-	-
	1.33N	440	-	-	-	-
	2.67N	563	-	-	-	-
$(CH_3)_4N.OH$	.67N	203	205	206	-	-
	1.33N	334	333	339	-	-
	2.67N	424	421	430	-	-


VELOCITY CONSTANT.
600
500
400
300
200
CONCENTRATION OF BASE.
·01 N
·02 N
·03 N
·04 N
·05 N
·06 N
·07 N
·08 N
·09 N
·10 N.
Ca(OH)₂ + 4% HCHO.
Sr(OH)₂ + 4% HCHO.
Ba(OH)₂ + 4% HCHO.
NaOH + 4% HCHO.
Ca(OH)₂ + 2% HCHO.
Sr(OH)₂ + 2% HCHO.
Ba(OH)₂ + 2% HCHO.
NaOH + 2% HCHO.
(CH₃)₄N·OH + 2% HCHO.

While uncertainty attaches to the values of the " constants " to be taken at very low concentrations of base, the graphs show, without doubt, the similarity in the action of the various bases. The constant appears in every case to pass through a minimum at a base concentration of approximately .01N to .02N. As to the meaning of these curves, nothing further will be said; it is sufficient, for the present purpose, to show that the constants for sodium hydroxide rise with increasing base concentration from .02N upwards, just as do those for the alkaline earths, and that the rate of increase of the constants is greater for the hydroxides of barium, strontium and calcium, than for that of sodium.

How then is the increase in the velocity constants with increasing base concentration to be explained? None of the explanations advanced for sodium hydroxide are of any use, except these which suppose the unionised base or formaldehyde salt to be the medium of change. With rising concentration of base, the concentrations of unionised base and salt would increase. It was impossible in the study of sodium hydroxide to investigate these further, on account of the great degree of ionisation of the base and salt, and consequent uncertainty with regard to the concentration of the unionised portions.

However, it should be possible to measure with greater accuracy the fractions ionised and unionised, when/

when dealing with derivatives of the alkaline earths, and thus the previous difficulty in the way of testing these theories is removed. Unfortunately, although one stumbling block has been removed, another has made its appearance. It is extremely difficult, - in fact quite impossible at present, - to settle the correct hydrolysis equations and constants for the formaldehyde salt of a diacid base, at the various concentrations employed. This means that it is impossible to determine the concentrations of total free base and aldehyde salt. A second trouble is that, though it were possible to settle these concentrations, it is very doubtful if an equilibrium equation could be found to give, even approximately,the influence of the common ions present on the degree of ionisation of the base and salt. It is thus evident that the suggested explanations of the increase in constants with increasing base concentration cannot be tested by the application of equations such as these given on pages 73 and 74.

However, other evidence can be brought forward in support of the general theory that the reaction, in all these cases, involves unionised molecules, either of the base or salt. The influence of neutral salts is, on the surface, in favour of this suggestion. In practically every case where an increase in the concentration of unionised molecules would be expected, a rise in the constants is found. The figures obtained are as follows.

NaOH Salts.

Conc. HCHO.	Conc. NaOH.	Constant, no salt.	Salt added.	Norm-ality.	Constant obtd.
1.33N	.04N	335	NaCl	.5N	356
			NaCl	1.0N	378
			NaCl	2.0N	416
			NaBr	.5N	351
			NaBr	1.0N	367
			NaBr	2.0N	419
			NaBr	3.0N	474
			NaBr	4.0N	529
			NaI	1.0N	372
			KCl	.5N	336
			KCl	1.0N	370
			KCl	2.0N	405
			LiCl	1.0N	379
			$NaNO_3$	1.0N	369
			Na_2SO_4	1.0N	360
			Sod.Acetate	1.0N	366
			Sod.Formate	.7N	346
			Sod.Succinate	1.0N	317
			Sod.Citrate	1.0N	314

$Ba(OH)_2$ Salts.

1.33N	.04N	383	NaCl	1.0N	395
			$BaCl_2$	.5N	514
			$BaCl_2$	1.0N	605
			$BaBr_2$	1.0N	618
			Ba.Acetate	1.0N	540
			Ba.Acetate	2.0N	692

$Ca(OH)_2$ Salts.

1.33N	.02N	440	NaCl	1.0N	400
			$BaCl_2$	1.0N	609
			$SrCl_2$	1.0N	642
			$CaCl_2$	1.0N	836
			$CaCl_2$	2.0N	998

Exper.	Conc. HCHO.	Conc. of Base.		
		.02N	.04N	.08N
NaOH N.NaCl.	.67N	236	228	266
	1.33N	370	375	391
	2.67N	451	458	479
$Ba(OH)_2$ $N.BaCl_2$	.67N	362	413	468
	1.33N	587	607	654
	2.67N	806	835	863

Neutral salt action may not, however, be due to its producing an increase in the concentration of un-ionised molecules - most likely it is not.[1] The evidence just given is, therefore, by no means sufficient. The rise in the constants with increasing base concentration might be explained by the neutral salt action- whatever it is- of the formaldehyde salt present. The greater rate of increase shown by the alkaline earths over the alkalies would be due to the greater salt action of derivatives of the first class over those of the second.

The theory that the unionised molecules of all these bases have the same effect in promoting the reaction studied, and that an increase in the concentration of these molecules is <u>alone</u> responsible for a rise in the constants,must be criticised on the following grounds. There is a rise in the constants with increasing base concentration for barium, strontium and calcium hydroxides, each considered separately, but there is also an increase in the constants as one proceeds from barium through strontium to calcium. Now, strontium and calcium hydroxides are, as far as can be said from the available data, practically equally ionised, and, accordingly, corresponding solutions should contain the same concentration of unionised molecules. It is evident that the increase in the constants cannot be satisfactorily explained merely by a decrease in the ionisation of the base. The suggestion that the increase is due to neutral salt action/

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1) eg, Noyes and Falk, J. Amer.Chem.Soc.,(1912),<u>34</u>,454.

action would remove this difficulty. It is only necessary to assume a greater salt action for calcium salts than for those of strontium.

Some evidence that the increase in the constants, with rising concentration of base, might be due to the neutral salt action of the unionised formaldehyde salt present in the solution, is afforded by a study of the velocity constants of the action of sodium hydroxide on formaldehyde, in presence of varying concentrations of sodium bromide.

Conc. NaBr added.	Conc. $Na^{\cdot}=Br'$ (50°C.)	Conc. NaBr (undiss)	Constants.	
			No salt.	Plus Salt.
.5N	.465N	.035N	335	335 + 17
1.0N	.67N	.33N		335 + 32
2.0N	1.08N	.92N		335 + 85
3.0N	1.50N	1.50N		335 + 138
4.0N	1.91N	2.09N		335 + 195

The rise in the constant appears to be very nearly proportional to the concentration of unionised neutral salt present.

Equally strong evidence against the rise in constants being due to neutral salt action is obtained from a study of the constants for barium and strontium hydroxides. If strontium salts have a greater neutral salt action than barium salts, why is the rate of increase of the constants for strontium hydroxide not considerably greater than that for barium hydroxide?

Taking everything into consideration, it seems that the observed increases would be better explained by, 1) assigning/

1) assigning to some derivative of the base a catalytic activity, characteristic of the base, and increasing in magnitude from sodium, through barium and strontium, to calcium.

2) assuming a neutral salt action of some derivative of the base, eg. the unionised formaldehyde salt. The first assumption would explain the rise in constants in passing from barium to strontium to calcium, while the second would give a reason for the variation in constants with experiments with any one base.

The alkaline earths have not given any definite information as to the mechanism of the reaction. There is a considerable difference between these and weak organic bases, and it was thought quite possible that a study of the latter would yield valuable results. The discussion will now be taken up from this point of view.

ORGANIC BASES.

Only tertiary organic bases will be considered. Tetramethylammonium hydroxide is so similar to the alkalies that it has been dealt with along with these. Primary and secondary bases combine with formaldehyde, and, owing to the disturbance thus introduced, constants obtained with these will not be employed to settle the points in question.

The tertiary bases used were trimethylamine and tetramethylethylenediamine. Trimethylamine is so volatile/

volatile that the experiments had to be performed in sealed tubes. The procedure was as follows. The required amounts of base and aldehyde were mixed at low temperatures, and a known volume, approximately 10 cc., of this solution was measured into several different tubes. The tubes were sealed, and placed in the thermostat at 50°C. At various intervals one tube was removed, cooled in ice water, opened and the contents washed into a known excess of .02N hydrochloric acid. The unused acid was estimated with .02N sodium hydroxide. The following experiments showed that, as far as volatilisation was concerned, the method of working was suitable.

Time in thermostat.	Vol .02N HCl required.
0 mins.	19.75 cc.
60 mins.	19.68 cc.
120 mins.	19.72 cc.
240 mins.	19.70 cc.
360 mins.	19.78 cc.

The experiments with tetramethylethylenediamine *were carried out in tightly corked boiling tubes, the corks being removed for the withdrawal of a sample for analysis. The base remaining was titrated directly with .02N hydrochloric acid, cresol red being used as indicator. That this procedure was satisfactory was shown by the following volatilisation experiment.

Time in thermostat.	Vol .02N HCl required.
0 mins.	9.53 cc.
33 mins.	9.55 cc.
88 mins.	9.48 cc.

The results obtained with these two bases are given in the table below. As the " constants " fall rapidly during an experiment, the values included in the table are those obtained by extrapolating to zero time.

Conc. of HCHO.	Concentration of Base.					
	$(CH_3)_3N$.			$(CH_3)_2N(CH_2)_2N(CH_3)_2$		
	.02N	.04N	.08N	.02N	.04N	.08N
.67N	21	15	11	-	20	-
1.33N	37	27	21	40	32	24
2.67N	86	62	44	-	50	-

Although, on account of difficulty in titration, the results for tetramethylethylenediamine can only be taken as approximately correct, it appears that the number of basic groups in the molecule has very little effect, the introduction of a second tertiary nitrogen does not double the constant obtained. The constants for both bases fall with increasing concentration of base, and the fall is roughly the same under the same conditions. This might be taken as some proof that the rise in constants with increasing base concentration in the case of barium, strontium and calcium hydroxides is not a direct consequence of the diacid character of these bases.

The fall in the constants with increasing base concentration at once suggests that it is not the unionised molecules of the base that are bringing about the change, but rather the ions formed from the base. (eg. The trimethylamine in solution will give rise to the/

the ions $(CH_3)_3NH^{\cdot}$, and OH', ie. the trimethyl-ammonium and hydroxyl ions.) The expression for the rate of the reaction will then be,

$$\begin{aligned} \text{Rate} &= k.[HCHO]^y[\text{Ion of base}] \\ &\quad k.[HCHO]^y\, m.[\text{Free base}] \\ &\quad K.[\text{Free base}] \\ &\quad K.[\text{Total base}] \end{aligned}$$

as the base-formaldehyde salt is approximately 98% hydrolysed. Since the acid and base are both weak, n, the hydrolysed fraction, is given by the expression,

$$\frac{n}{1-n} = \sqrt{\frac{K_w}{k_a\, .k_b}}$$

At 50°C. the values are,

$$= \sqrt{\frac{6.5\times10^{-14}}{13\times10^{-14}\times1.5\times10^{-4}}}$$

$$\therefore \underline{n = .98}$$

The above formula for the rate is valid as the change is undoubtedly monomolecular with respect to the base; the reason for the fall in the " constant " during an experiment will be discussed later, (page 97). From this equation, for a given concentration of formaldehyde

$$K_1/K_2 = m_1/m_2$$

As these are weak bases, the equilibrium between the ions and unionised molecules obeys the mass action law, and accordingly

$$\frac{m^2}{(1-m).v} = \text{Constant.}$$

As/

As m is very small, $m \propto \sqrt{v}$,

and thus,

$$K_1/K_2 = \sqrt{v_1}/\sqrt{v_2}$$

If, then, the trimethylammonium or hydroxyl ions are one of the reactants, values calculated from this last equation by substituting volumes corresponding to the concentrations of base used, should bear the same ratio to each other as do the values in the table on page 94. The results obtained when the values for .02N base are made equal to those in the corresponding position in the table mentioned, are given below.

Conc. of HCHO.	Concentration of Base. $(CH_3)_3N$. .02N	.04N	.08N	$(CH_3)_2N(CH_2)_2N(CH_3)_2$ .02N	.04N	.08N
.67N	21	15	10	-	-	-
1.33N	37	26	19	40	28	20
2.67N	86	61	43	-	-	-

The results for tetramethylethylenediamine do not show such good agreement as do these for trimethylamine, but this is not to be wondered at, considering the difficulties experienced in the titration of the base.

These results prove that tertiary organic bases take part in this reaction in the ionised state. That it is the hydroxyl ion that reacts is readily proved, as the addition of the other ion in excess, in the form of the hydrochloride of the base, reduces the constant greatly. The effect of the hydrochloride is to increase the concentration of the complex organic ion, but to diminish that of the hydroxyl ion. As an example/

example, the figures for trimethylamine are given.

HCHO - 1.33N,+ $(CH_3)_3N$ - .04N, Constant = 27.
As above,+ $(CH_3)_3N.HCl$ - .04N, Constant = 8.

As a natural consequence of this, the velocity constant should fall during a single experiment, as a highly ionised salt of the base is produced in the reaction. This fall is quite distinct in all the experiments performed, (cf. pages 115 and 127).

From the equation for the rate of the reaction given on page 95, for a definite concentration of base,

$$\frac{K_1}{K_2} = \frac{k.[HCHO_1]^y.m_1}{k.|HCHO_2|^y.m_2}$$

m_1 and m_2 will be equal as there is practically no unhydrolysed salt present, and, therefore,

$$\frac{K_1}{K_2} = \frac{[HCHO_1]^y}{[HCHO_2]^y}$$

Solving for y,

$$y = \frac{\log K_1 - \log K_2}{\log[HCHO_1] - \log[HCHO_2]}$$

This equation will now be applied to the constants for .08N trimethylamine, (page 94), as being those most accurately determined.

When the concentration of total formaldehyde is used, and K_1 and K_2 have the values -

(11 and 21) $y = .943$
(21 and 44) $y = 1.062$
Average $y = \underline{1.002}$

The results/

results obtained when the concentrations of hydrated simple formaldehyde molecules are substituted, are not so good, (1.01 and 1.3), but these concentrations are themselves doubtful, and there is, in this case, no reason for supposing one form of the aldehyde to be more active than another. It may be taken, then, that formaldehyde enters into the velocity equation to the first power.

These observations may be extended. It seems justifiable to say that tertiary organic bases react with formaldehyde in virtue of their hydroxyl ion concentration, and that one molecule of base reacts with one molecule of aldehyde.

Thus far all appears to be satisfactorily explained on the assumption that the hydroxyl ions are the form in which the base takes part in the reaction. There is, however, one difficulty which arises, - the effect of sodium chloride and calcium chloride on trimethylamine is to raise the constant enormously.

HCHO-1.33N,+$(CH_3)_3$N-.04N,		Constant	= 27
"	" +NaCl- 1.0N.	"	= 68
"	" +$CaCl_2$,1.0N.	"	= 158

This does not invalidate what has been said, but is rather a point for which an explanation has still to be found. Various explanations might be advanced for this curious behaviour. A study of the increase in constants under the influence of neutral salts leads to the conclusion that the matter cannot be satis-factorily/

satisfactorily explained by neutral salt action.

It might be suggested that small amounts of sodium and calcium hydroxides are formed, potentially at least, and that these more active bases give rise to increased constants. Evidence against this explanation may be obtained from the graphs on page 86. These show that, as the concentration of base decreases, the constant passes through a minimum and then rises again very rapidly. The minimum values are for

$NaOH + 1.33N\ HCHO = 323$
$Ca(OH)_2 + 1.33N\ HCHO = 440$

and, consequently, this provides no explanation.

However, these curves might be taken as showing that there are really two separate reactions, one preponderating at low concentrations of base, and giving a constant decreasing with rising concentration of base, the other being the more important in concentrated solution, and giving a rising constant. The minimum on the curves would be produced by a combination of the two. Should the reaction, which is the controlling one in high base concentrations, fall off rapidly below concentrations of .02N, the suggested activity of sodium and calcium hydroxides might quite well explain the observed constants.

Another explanation could be found in a specific catalytic action of the metallic ions,- independent of the concentration of the ion. Such an effect has been suggested previously, (pages 73 and 92). If it be supposed that sodium and calcium hydroxides are formed in/

in such small quantity that their effect may be neglected, the following calculation can be made.

Base.	Salt added.	Constant- no salt.	Constant- with salt.	Catalytic effect.
$(CH_3)_3N$	N.NaCl	27	68	41
"	N.$CaCl_2$	27	158	131
TME.Diamine	N.$CaCl_2$	32	173	141

While the figures for tetramethylethylenediamine are always open to doubt, on account of difficulty in titration, the catalytic effect deduced from the experiment quoted, agrees very well with that obtained by using trimethylamine.

Further investigation along these lines leads to very interesting results. If it be supposed that the catalytic action is independent of the concentration of the metallic ion, 41 may be subtracted from any constant obtained with sodium hydroxide as the base, and similarly 131 from values obtained with calcium hydroxide. This gives the following results:-

Conc. HCHO.	Consts.uncorrected.		Consts.corrected.	
	NaOH	$Ca(OH)_2$	NaOH	$Ca(OH)_2$
.67N	205	288	164	157
1.33N	335	440	294	309
2.67N	442	563	401	432

The corrected results are seen to be very similar. Constants of the same order can be obtained for barium and strontium hydroxides by subtracting 70 and 90 respectively, so that the series becomes:-

Constants actually obtained in the experiments, for .02N base.

Conc. HCHO.	NaOH.	$Ba(OH)_2$	$Sr(OH)_2$	$Ca(OH)_2$
.67N	205	232	248	288
1.33N	335	367	392	440
2.67N	442	460	470	563
Catalytic Effect.	41	70	90	131

Constants thus corrected.

Conc. HCHO.	NaOH.	$Ba(OH)_2$	$Sr(OH)_2$	$Ca(OH)_2$
.67N	164	162	158	157
1.33N	294	297	302	309
2.67N	401	390	380	432

Taking into account the possible errors, it seems that the constants thus obtained approximate to 160, 300 and 400 in all cases, and this indicates that the mechanism of reaction of the various strong inorganic bases is essentially the same,- a conclusion already arrived at on other grounds, (pp. 83-87).

It is not necessarily the metallic ions that exert the catalytic effect. It cannot be hydroxyl ions, as they are present even in the trimethylamine solutions giving small constants, and, on adding the salt, any strong base formed could not possibly give a concentration of hydroxyl ions greater than that given by the trimethylamine. It might, however, be the unionised molecules of the strong inorganic bases. The effect of sodium and calcium chlorides on trimethylamine would thus/

thus be due to the traces of unionised sodium and calcium hydroxides formed.

The evidence given by the various bases will now be discussed as a whole, and any possible conclusions drawn from the facts presented.

CONCLUSION.

The most definite information as to the mechanism of their action has been given by the weak organic bases. As far as concerns that stage of the reaction to which the velocity constants observed refer, tertiary organic bases react with formaldehyde in virtue of their hydroxyl ion concentration, and one molecule of base reacts with one of aldehyde. There may be other stages in the change, but they must be infinitely fast compared with the one measured. This would suggest that the reaction takes a course such as,

$$HCHO + OH' = HCOO' + 2H \quad \text{(Slow)}$$
$$HCHO + 2H = CH_3OH \quad \text{(Fast)}$$

There is a considerable amount of evidence in favour of such a course,(cf.page 31).

Evidence as to the mechanism of the reaction is by no means so clear when the strong inorganic bases are considered. That it is essentially the same with the alkalies and the alkaline earths is proved by conductivity and other measurements,(pages 83-87). The increasing irregularity in the monomolecular constants/

constants with increase in the ratio of base to aldehyde, especially noticeable for barium and strontium hydroxides, suggests that the concentration of formaldehyde is becoming insufficiently great to keep the reaction apparently monomolecular, and indicates that the strong inorganic bases play a direct part in the change, and are not removed in some secondary way. The velocity constants for these bases rise both with increasing concentration of aldehyde and of base. The rate of increase in the first case, is not proportional to any integral power of the formaldehyde concentration,- even when allowance is made for various disturbing factors, such as active forms of the aldehyde and base.

Several attempts have been made to explain the increase in constants with increasing concentration of base. Naturally, the first suggestion is that the activity of the base is due to its concentration of unionised molecules, and this is favoured, in a general way, by the effect of neutral salts on the velocity of the reaction.

The proposal that the unionised molecules of all the strong inorganic bases have the same specific effect in promoting the reaction studied, and that an increase in the concentration of these is alone responsible for a rise in the velocity constants is disproved by the behaviour of strontium and calcium hydroxides.

Neutral salt action of the unionised formaldehyde salt present might be given as an explanation of the increase/

increase in constants with rising concentration of each individual strong inorganic base, and also of the variation in these in passing from one such base to another. There is a certain amount of evidence in favour (page 91), but the proposal is considered to be, in itself, insufficient.

The study of the velocity constants obtained with these inorganic bases, leads to the conclusion that some derivative of the base exerts a catalytic effect, characteristic of the base, and increasing in magnitude from sodium, through barium and strontium, to calcium. Experiments with trimethylamine, (pages 98-101), give strong, and quite independent, support to this conclusion. It is possible, from results obtained with this weak organic base to give a relative value to the catalytic effect exerted by the derivatives of the strong inorganic bases. On subtracting the appropriate catalytic figure from the constants given by the strong inorganic bases, values are obtained which are practically identical for all these bases - at corresponding concentrations of base and aldehyde. This leads to the conclusion,- already reached on other grounds, (pages 83-87),-that the mechanism of reaction of the various strong inorganic bases is essentially the same.

It is difficult to settle what derivative of the inorganic base is responsible for the catalytic effect. As has been proved on page 101, it is certainly not hydroxyl/

hydroxyl ions. A consideration of the various possible catalysts shows that the most probable are the metallic ions, and the unionised molecules of free inorganic base.

Owing to difficulty in the determination of the hydrolysis constant of a diacid base, it is impossible to give an equation representing the behaviour of the alkaline earths in their action on formaldehyde, but a formula can be suggested for the alkalies, to represent roughly the state of affairs found in practice. If it be supposed that the reaction is primarily due to hydroxyl ions, and that the catalytic effect is caused by unionised molecules of the free inorganic base, and that the effect is proportional to the concentration of these molecules, then,

$$\text{Rate} = (A + B)[\text{Total Base}]$$

where,

$$A = \frac{k.h.m.[HCHO]^y}{[HCHO] + h}$$

$$B = \frac{K.h.(1-m)}{[HCHO] + h}$$

where,

k = fundamental velocity constant of reaction.
K = catalytic effect of unionised molecules of base.

The observed velocity constants would be the sum of these two, ie.

$$\frac{h}{[HCHO]+h}\left\{ m.(k.[HCHO]^y - K) + K \right\}$$

If the concentration of base be increased, - that of formaldehyde/

formaldehyde remaining constant,- m will decrease slightly, and, if it be assumed that K is greater than $k.[HCHO]^y$, then a smaller and smaller quantity has to be subtracted from K and, therefore the constant increases. This expression would also give a qualitative explanation of the effect of increasing the concentration of formaldehyde, while keeping that of the base fixed. This equation,

$$\text{Rate} = \left\{ \frac{k.h.m.[HCHO]^y}{[HCHO] + h} + \frac{K.h.(1-m)}{[HCHO] + h} \right\} [\text{Total Base}]$$

also expresses the results obtained with the weak organic bases, as the catalytic effect, K , is equal to zero, and the first term simplifies to $(km[HCHO]^y)$, since the formaldehyde salt is practically completely hydrolysed.

ie. $$\text{Rate} = \left\{ k.m.[HCHO]^y \right\} [\text{Total Base}]$$
(cf. page 95).

While this equation is merely a suggestion, it serves to show that there is no reason why the mechanism of the reaction between the strong inorganic bases and formaldehyde should not be fundamentally identical with that of the weak organic bases. It must be admitted that the inorganic bases have given very little definite information on which to found an argument, but, taking everything into consideration, it would seem that both react with formaldehyde in virtue of their hydroxyl ion concentration, but that, in addition, the strong inorganic bases possess a catalytic power characteristic of each individual base.

INDEX TO EXPERIMENTAL DATA.

Page.

Reaction Velocity Experiments:-

Neutral Salt Action:-

For information as to calculation of results, see p.18.

LITHIUM HYDROXIDE.

HCHO 2%.(.67N).

LiOH.	t.	a.	a - x.	$k.10^5$	Average.
.02N	29	9.21	7.90	230	
	60		6.80	220	225
	102		5.40	227	
	140		4.52	221	
.04N	31	19.06	16.30	219	
	60		13.93	227	215
	121		10.66	209	
	180		8.20	204	
.08N	33.5	39.10	32.75	230	
	60		28.62	226	223
	90		24.60	224	
	138		19.90	213	

HCHO 4%.(1.33N).

.02N	31	8.90	7.11	315	
	60		5.60	335	333
	102		4.03	337	
	142		2.87	346	
.04N	30	18.70	14.75	343	
	60		11.70	339	336
	120		7.48	332	
	181		4.74	329	
.08N	32	38.75	29.95	350	
	63		23.35	349	345
	90		19.00	344	
	150		12.20	335	

HCHO 8%.(2.67N).

.02N	33	8.67	6.30	420	
	60		4.77	433	435
	103		3.10	434	
	143		1.95	453	
.04N	30	18.36	13.55	440	
	60		9.94	444	435
	120		5.54	434	
	181		3.14	424	
.08N	30.5	38.15	27.90	446	
	64		19.85	443	438
	90		15.42	437	
	150		8.73	427	

SODIUM HYDROXIDE.

HCHO 2%. (.67N).

NaOH.	t.	a.	a - x.	$k.10^5$	Average.
.02N	30	9.20	8.00	202	205
	60		6.80	219	
	120		5.27	202	
	180		4.05	198	
.04N	30	19.10	16.57	206	199
	60		14.42	203	
	120		11.15	195	
	180		8.66	191	
.08N	30	38.80	33.49	213	207
	60		28.90	213	
	120		22.02	205	
	180		17.11	197	

HCHO 4%. (1.33N)..

.02N	30	8.98	7.15	330	335
	60		5.49	356	
	120		3.57	334	
	180		2.37	322	
.04N	30	18.83	15.09	321	325
	60		11.90	332	
	120		7.62	327	
	180		5.00	320	
.08N	30	38.30	30.18	345	336
	60		23.80	344	
	120		15.30	332	
	180		10.11	321	

HCHO 8%. (2.67N).

.02N	33	8.86	6.33	443	442
	60		4.82	441	
	120		2.67	434	
	180		1.38	449	
.04N	30	18.42	13.60	439	433
	60		10.00	442	
	120		5.62	430	
	180		3.20	422	
.08N	60	37.90	20.44	447	438
	120		11.37	436	
	180		6.39	430	

POTASSIUM HYDROXIDE.

KOH.	t.	a.	a - x.	$k.10^5$	Average.
		HCHO 2%, (.67N)			
.02N	30	9.20	7.98	206	
	60		6.84	215	202
	120		5.35	196	
	180		4.15	192	
		HCHO 2.68%. (.90N)			
.04N	30	18.38	15.30	266	
	60		12.74	265	258
	120		9.16	252	
	180		6.53	250	
		HCHO 2.68%. (.90N)			
.08N	33	38.20	30.78	285	
	78		23.47	271	267
	128		17.80	259	
	180		13.40	253	
		HCHO 4%, (1.33N)			
.02N	40.5	8.82	6.32	358	
	77		4.90	332	338
	148		2.84	333	
	217		1.70	330	
		HCHO 5.36%, (1.80N)			
.04N	30	18.14	13.90	385	
	60		10.64	386	383
	120		6.32	382	
	180		3.77	379	
		HCHO 5.36%, (1.80N)			
.08N	30	38.06	28.96	396	
	60		21.75	405	393
	120		12.87	392	
	180		7.87	380	
		HCHO 8%, (2.67N)			
.02N	30	8.55	6.35	431	
	60		4.66	439	433
	120		2.64	425	
	180		1.40	437	
		HCHO 10.72%, (3.60N)			
.04N	30	17.40	12.72	453	
	60		9.21	460	460
	120		4.84	463	
	180		2.56	462	
		HCHO 10.72%, (3.60N)			
.08N	30	36.96	26.77	467	
	60		19.50	463	462
	120		10.32	462	
	180		5.56	457	

TETRAMETHYLAMMONIUM HYDROXIDE.

HCHO .67N.

$(CH_3)_4NOH$.	t.	a.	a - x.	$k.10^5$	Average.
.02N	32.5	9.10	7.75	214	203
	68		6.64	201	
	125		5.06	204	
	405		1.49	194	
.04N	33	18.24	15.52	212	205
	67		13.18	211	
	126		10.03	206	
	405		3.08	191	
.08N	32	36.32	30.77	225	206
	66		26.04	219	
	127		20.64	193	
	405		6.46	185	

HCHO 1.33N.

.02N	31.5	8.91	6.98	337	334
	62		5.57	329	
	89		4.51	332	
	119		3.53	338	
.04N	35	17.70	13.48	338	333
	64		10.80	335	
	90		8.92	331	
	120		7.17	327	
.08N	37	35.20	26.25	344	339
	65		21.16	340	
	91		17.42	336	
	120		13.99	334	

HCHO 2.67N.

.02N	35.5	8.05	5.73	416	424
	64		4.33	421	
	90		3.34	425	
	120		2.43	434	
.04N	31.5	18.48	13.60	423	421
	60		10.35	420	
	86		8.03	421	
	116		6.00	421	
.08N	30.5	18.10	13.32	437	430
	58		10.24	427	
	85		7.83	428	
	114		5.92	426	

(5 cc. each time).

BARIUM HYDROXIDE.

HCHO (.67N).

$Ba(OH)_2$	t.	a.	a - x.	$k.10^5$	Average.
.02N	30.5	9.15	7.74	238	
	60		6.56	241	232
	121		4.90	224	
	180		3.57	227	
		HCHO (.67N).			
.04N	28.5	18.60	15.66	262	
	96		10.89	242	245
	134		8.83	241	
	180		7.02	235	
		HCHO (.60N).			
.08N	30	39.95	32.55	296	
	60		27.06	282	272
	120		19.50	260	
	180		14.27	248	

		HCHO (1.33N).			
.02N	30	8.90	6.83	383	
	60		5.37	366	367
	120		3.30	359	
	181		1.98	361	
		HCHO (1.33N).			
.04N	30	18.35	13.97	395	
	98		7.72	384	383
	134		5.75	376	
	180		3.88	375	
		HCHO (1.20N).			
.08N	30	40.50	30.10	430	
	60		22.60	422	406
	120		13.61	395	
	180		8.52	376	

		HCHO (2.67N).			
.02N	30	8.65	6.38	441	
	60		4.59	459	460
	120		2.37	469	
	184		1.18	470	
		HCHO (2.67N).			
.04N	30	18.10	12.88	492	
	101		6.06	471	479
	135		4.12	476	
	183		2.41	478	
		HCHO (2.40N).			
.08N	30	39.15	27.40	516	
	60		19.08	520	507
	120		9.79	502	
	180		5.11	491	

STRONTIUM HYDROXIDE.

HCHO .67N.

$Sr(OH)_2$	t.	a.	a - x.	$k.10^5$	Average.
.02N	30	9.05	7.53	266	
	76		5.92	243	248
	143		4.15	237	
	199		2.95	245	
.04N	33	18.32	14.81	280	
	63		12.23	279	272
	110		9.29	268	
	149		7.49	261	
.08N	27	38.08,	30.37	(364)	
	70		22.50	326	307
	114		17.05	306	
	204		9.84	288	

HCHO 1.33N.

.02N	30	8.84	6.71	399	
	60		5.06	404	392
	145		2.48	381	
	202		1.49	383	
.04N	30	18.20	13.87	393	
	69		9.56	405	393
	110		6.85	386	
	154		4.58	389	
.08N	29	38.08	27.37	494	
	75		17.24	459	450
	119		11.67	432	
	210		5.15	414	

HCHO 2.67N.

.02N	30	8.40	6.08	468	
	60		4.38	471	470
	150		1.66	470	
	205		.90	473	
.04N	30	18.35	12.96	504	
	60		9.30	492	494
	125		4.47	491	
	166		2.84	488	
.08N	33.5	37.67	24.50	558	
	70		15.74	541	544
	120		8.61	534	
	215		2.88	542	

CALCIUM HYDROXIDE.

HCHO .67N.

$Ca(OH)_2$	t.	a.	a - x.	$k.10^5$	Average.
.02N	31	8.93	7.15	312	
	62		5.96	283	288
	120		4.16	277	
	176		2.87	280	

HCHO 1.33N.

.02N	30	8.38	6.14	450	
	60		4.60	434	440
	122		2.54	425	
	180		1.29	451	

HCHO 2.67N.

.02N	30	8.13	5.43	584	
	60		3.80	550	563
	127		1.61	554	
	180		.78	565	

TRIMETHYLAMINE.

HCHO .67N.

$(CH_3)_3N$.	t.	a.	a - x.	k.10^5.	k.10^5(t=0).
.02N	60	9.93	9.64	21.3	
	120		9.42	19.0	21.5
	210		9.00	20.3	
	330		8.64	18.3	
.04N	60	19.74	19.39	13.0	
	150		18.74	15.1	15.4
	320		17.80	14.1	
	500		17.23	11.8	
.08N	60	35.56	34.96	12.2	
	150		34.21	11.2	11.5
	320		33.15	9.5	
	500		32.13	8.8	

HCHO 1.33N.

.02N	60	9.80	9.32	36.3	
	120		8.88	35.7	37.0
	240		8.13	33.8	
	360		7.58	31.0	
.04N	60	19.99	19.29	26.0	
	120		18.46	28.9	26.6
	240		17.37	25.5	
	360		16.47	23.4	
.08N	60	40.46	39.16	23.5	
	120		38.16	21.2	20.6
	240		36.41	19.1	
	360		35.13	17.0	

HCHO 2.67N.

.02N	60	9.54	8.61	74.2	
	120		7.95	65.9	86.0
	210		7.01	63.7	
	330		6.18	57.1	
.04N	60	19.48	18.06	54.8	
	120		16.94	50.5	62.0
	210		15.59	46.1	
	330		14.11	42.5	
.08N	60	39.85	37.68	40.5	
	120		36.01	36.7	44.0
	210		33.88	33.6	
	330		31.63	30.4	

Last column contains values of k.10^5, extrapolated for t = 0.

TETRAMETHYLETHYLENEDIAMINE.

HCHO .67N.

Base.	t.	a.	a - x.	k.10^5.	Value taken.
.04N	30	9.30	9.24	(9.3)	
	86		8.96	18.8	20
	136		8.71	20.9	

HCHO 1.33N.

Base.	t.	a.	a - x.	k.10^5.	Value taken.
.02N	52	4.40	4.20	39.	
	102		4.00	41.	40
	529		3.00	32.	
.04N	30	9.10	8.90	32.	
	85		8.54	32.	32
	136		8.28	30.	
.08N	52	18.70	18.00	32.	
	103		17.70	23.	24
	534		15.20	17.	

HCHO 2.67N.

Base.	t.	a.	a - x.	k.10^5.	Value taken.
.04N	30	8.84	8.54	50.	
	87		8.02	49.	50
	136		7.39	(57.)	

Reaction Velocity Experiments with high and low Concentrations of certain Bases.

SODIUM HYDROXIDE.

HCHO .67N.

NaOH.	t.	a.	a - x.	k.10^5.	Average.
.002N	43	2.90	2.18	288	
	118		1.54	(233)	270
	177		1.04	252	
.005N	40.5	7.50	6.01	238	
	126		3.87	228	225
	183		3.09	210	

SODIUM HYDROXIDE, (contd.)

HCHO 1.33N.

NaOH.	t.	a.	a - x.	$k.10^5$.	Average.
.002N	41	2.17	1.49	398	
	85		1.02	386	396
	169		.45	404	
.005N	42	6.71	4.69	370	
	86		3.37	348	362
	169		1.60	368	
.01N	43	15.40	11.02	338	
	88		7.94	327	336
	170		4.03	343	
.32N	34	6.19	4.17	505	
	80		2.72	446	476

TETRAMETHYLAMMONIUM HYDROXIDE.

HCHO .67N.

Base.	t.	a.	a - x.	$k.10^5$.	Average.
.002N	47	14.15	10.77	252	
	147		6.14	247	255
	269		2.70	267	

STRONTIUM HYDROXIDE.

HCHO .67N.

$Sr(OH)_2$	t.	a.	a - x.	$k.10^5$.	Average.
.002N	44.5	2.73	1.99	309	
	109		1.37	(275)	309
	168		.83	308	

HCHO 1.33N.

.0005N	43	0.67	0.285	863	
	92		0.000 (Just alkaline).	898	863
.001N	46	4.52	2.70	486	
	94		1.24	594	486
	152		.45	657	
.002N	45.5	2.35	1.44	467	
	100		.87	430	467
	176		.26	543	

SODIUM HYDROXIDE AND FORMALDEHYDE.

(Various concentrations of each. Figures used in drawing up TABLES 2 and 3, pages 40 and 41).

These experiments were performed in order to compare the constants obtained. As the constants given by certain formulae vary in magnitude according to the volume taken for analysis, and the normality of the acid used in the titration, these factors have been included in the following tables.

Conc. HCHO.	Conc. NaOH.	Vol. for analysis	Norm. of acid.	Time in mins.	Titration in cc.
.04N	.08N	10 cc.	.02N	0	38.65
				353	37.40
				944	35.86
				1643	34.60
				2520	33.60
				3911	32.00
				8345	28.83
				14045	29.00
				19857	29.29
				29772	29.70
.08N	.08N	10 cc.	.02N	0	38.20
				355	34.63
				941	30.57
				1647	28.00
				2525	25.88
				3875	23.94
				5341	22.70
				8349	20.90
				14020	19.54
				19863	18.67
				29793	18.10
.16N	.08N	10 cc.	.02N	0	38.35
				327	29.13
				928	21.00
				1620	16.35
				2515	13.05
				2831	12.14
				3848	10.14
				5315	8.22
				8342	5.79
				14042	3.90
				19862	2.85

Conc. HCHO.	Conc. NaOH.	Vol. for analysis.	Norm. of acid.	Time in mins.	Titration. in cc.
.32N	.16N	10 cc.	.137N	0	11.33
				39.5	10.00
				61	9.47
				84	8.98
				109	8.53
				142	7.92
				170	7.54
				191	7.22
				920	3.50
.64N	.32N	10 cc.	.137N	0	22.78
				34.5	17.56
				56.5	15.35
				79	13.80
				105	12.35
				138	10.98
				165	10.08
				178	9.75
1.28N	.64N	10 cc.	.500N	0	11.40
				32.7	7.05
				51	5.95
				74	4.96
				83	4.71
				102	4.19
				135	3.56
				159	3.26
2.56N	1.28N	5 cc.	.500N	0	10.87
				24.2	5.77
				43.7	4.30
				67	3.36
				96	2.60
				126	2.16
				152	1.88

NEUTRAL SALT ACTION.

Sodium Hydroxide and Salts.

Concentrations used:-

NaOH............0.04N.
HCHO............1.33N.

Normal Constant, (no salt present).....335.

SODIUM CHLORIDE.

Conc.	t.	a.	a - x.	$k.10^5$	Average.
.5N.	30	18.56	14.48	359	
	66		10.84	354	356
	97		8.34	358	
	135		6.22	352	
N.	35	18.90	13.76	394	
	65		10.58	388	378
	157		4.98	369	
	223		2.94	362	
2N.	38	18.50	12.70	430	
	63		10.08	419	416
	94		7.58	412	
	131		5.50	402	

SODIUM BROMIDE.

.5N.	39	18.53	13.44	358	
	71		10.37	355	351
	112		7.58	347	
	149		5.68	345	
N.	32.5	18.28	13.70	385	
	71		10.11	362	367
	116		6.96	362	
	166		4.67	357	
2N.	31	18.80	13.88	425	
	69		9.55	426	419
	102		7.10	415	
	151		4.52	410	
3N.	31	18.62	13.19	483	
	68		8.73	484	474
	100		6.24	475	
	148		3.97	453	
4N.	43.5	18.63	10.68	555	
	74		7.46	537	529
	116		4.57	526	
	149		3.37	498	

SODIUM IODIDE.

N.	61	17.92	10.40	388	
	110		6.97	373	372
	147		5.23	364	
	188		3.74	362	

POTASSIUM CHLORIDE.

Conc.	t.	a.	a - x.	$k.10^5$	Average.
.5N.	66	17.90	10.65	342	
	113		7.47	336	336
	151		5.60	334	
	190		4.22	330	
N.	30	18.46	14.12	388	
	67		10.47	368	370
	113		7.06	369	
	163		4.86	356	
2N.	27.5	18.66	14.29	422	
	63		10.38	404	405
	116		6.32	405	
	159		4.47	390	

LITHIUM CHLORIDE.

N.	33.5	18.55	13.70	393	
	73		9.81	379	379
	105		7.40	380	
	155		5.09	362	

SODIUM NITRATE.

N.	38	18.41	13.17	383	
	68		10.38	366	369
	100		7.93	366	
	132		6.17	360	

SODIUM SULPHATE.

N.	38	18.56	13.46	367	
	70		10.34	363	360
	104		7.95	354	
	134		6.18	356	

SODIUM ACETATE.

N.	37	18.00	12.95	387	
	66		10.17	376	374
	98		7.81	370	
	130		6.06	364	

SODIUM ACETATE (Contd.)

N.	44	18.33	12.60	370	
	86		8.90	365	358
	123		6.70	355	
	175		4.65	340	

Average of two......366

SODIUM FORMATE.

.67N.	34	18.86	14.19	364	
	62		11.46	349	346
	92		9.22	338	
	129		7.04	332	

SODIUM SUCCINATE.

N.	45	18.67	13.29	328	
	85		9.95	322	317
	126		7.43	318	
	172		5.67	301	

SODIUM CITRATE.

N.	42	18.25	13.17	338	
	82		10.00	319	319
	124		7.32	320	
	171		5.60	300	
N.	56	19.62	12.92	324	
	97		9.77	312	309
	136		7.63	302	
	176		5.85	299	

Average of two......314

Barium Hydroxide and Salts.

Concentrations used:-

$Ba(OH)_2$.......0.04N.
HCHO..........1.33N.

Normal Constant....................383.

SODIUM CHLORIDE.

Conc.	t.	a.	a - x.	$k.10^5$	Average.
N.	34.5	17.50	12.72	402	
	77		8.66	397	395
	115		6.25	389	
	171		3.76	390	

BARIUM CHLORIDE.

.5N.	27	18.18	13.00	540	
	66		8.30	516	514
	95		6.11	499	
	133		3.91	502	
N.	27.5	17.67	11.80	637	
	62		7.44	606	605
	105		4.28	587	
	157		2.11	588	

BARIUM BROMIDE.

N.	21	17.70	12.84	(664)	
	58		7.64	629	618
	88		5.10	614	
	125		3.06	610	

BARIUM ACETATE.

N.	31	18.17	11.53	(637)	
	67		7.94	537	541
	98		5.10	563	
	137		3.50	522	
2N.	29	17.95	10.18	(850)	
	71		5.70	702	692
	98		3.26	756	
	128		2.89	620	

Calcium Hydroxide and Salts.

Concentrations used:-

$Ca(OH)_2$........0.02N.
HCHO..........1.33N.

Normal Constant........................441.

SODIUM CHLORIDE.

Conc.	t.	a.	a - x.	$k.10^5$	Average.
N.	42	9.13	6.25	392	
	72		4.67	404	400
	115		3.22	394	
	146		2.30	410	

BARIUM CHLORIDE.

N.	36	8.90	5.34	616	
	68		3.47	602	609
	109		1.94	607	
	147		1.13	610	

STRONTIUM CHLORIDE.

N.	32	8.85	5.44	660	
	67		3.35	630	642
	123		1.50	627	
	159		.82	650	

CALCIUM CHLORIDE.

N.	26	8.88	5.32	856	
	62		2.70	834	836
	100		1.31	831	
	140		.63	821	
2N.	28	8.52	4.40	1024	
	63		2.01	996	998
	102		.82	997	
	142		.35	976	

Sodium Hydroxide and Formaldehyde.....Various Concs.
Sodium Chloride......................Normal.

HCHO .67N.

NaOH.	t.	a.	a - x.	$k.10^5$	Average.
.02N	25	9.29	8.09	240	236
	61		6.66	237	
	94		5.59	235	
	165		3.46	232	
.04N	54	18.30	13.80	227	228
	86		11.53	233	
	120		9.80	226	
	188		6.91	225	
.08N	39.5	38.40	29.80	279	266
	75		24.03	271	
	165		14.97	248	

HCHO 1.33N.

.02N	32.5	9.28	6.98	380	370
	62		5.47	370	
	92		4.24	370	
	188		1.97	358	
.04N	35	17.70	12.94	389	375
	72		9.44	379	
	135		5.66	367	
	197		3.36	366	
.08N	35.5	38.03	27.07	416	391
	70		19.87	403	
	161		9.42	376	
	265		3.97	370	

HCHO 2.67N.

.02N	42	8.44	5.52	439	451
	69		4.14	448	
	160		1.55	460	
	191		1.13	457	
.04N.	37	18.09	12.24	458	458
	65		9.08	461	
	153		3.59	459	
	185		2.63	453	
.08N	32	36.00	25.08	491	479
	60		18.29	490	
	148		7.25	470	
	189		4.78	464	

Barium Hydroxide and Formaldehyde.....Various Concs.
Barium Chloride.......................Normal.

HCHO .67N.

$Ba(OH)_2$	t.	a.	a - x.	$k.10^5$	Average.
.02N	54	8.25	5.21	370	362
	87		4.04	357	
	118		3.10	360	
	185		1.79	359	
.04N	21.3	16.67	13.61	414	413
	48		10.64	422	
	81		7.88	402	
	178		3.62	(373)	
.08N	43.7	35.64	21.14	519	468
	78		15.03	481	
	100		12.48	456	
	169		7.12	414	

HCHO 1.33N.

.02N	48.5	8.17	4.16	604	587
	81		2.80	574	
	112		1.82	582	
	179		.73	586	
.04N	27.3	17.67	11.80	642	607
	62		7.44	606	
	104		4.28	592	
	157		2.11	588	
.08N	29.5	30.08	18.67	702	654
	65		11.19	661	
	87		8.22	647	
	154		3.53	604	

HCHO 2.67N.

.02N	32	7.55	4.14	816	806
	62		2.42	797	
	134		.56	(843)	
	165		.23	(919)	
.04N	31	17.40	9.66	824	835
	60		5.60	821	
	143		1.11	836	
	182		.48	857	
.08N	29	35.50	19.29	914	863
	58.5		11.00	870	
	141		2.36	835	
	179		1.15	832	

ORGANIC BASES AND SALTS.

1, TRIMETHYLAMINE.

Concentrations used:-

$(CH_3)_3N$..............0.04N.
HCHO................1.33N.

Normal Constant, (t = 0).......................26.6

SODIUM CHLORIDE.

Conc.	t.	a.	a - x.	$k.10^5$	(t = 0)
N.	60	19.53	18.00	59.0	
	150		16.34	51.6	68
	320		14.02	45.0	
	500		12.15	41.2	

CALCIUM CHLORIDE.

Conc.	t.	a.	a - x.	$k.10^5$	(t = 0)
N.	60	18.48	15.03	150	
	150		11.77	131	158
	320		8.42	107	
	500		6.04	97	
N.	60	19.16	15.73	143	
	120		13.34	131	
	180		11.43	125	
	244		9.90	117	

TRIMETHYLAMINE HYDROCHLORIDE.

Conc.	t.	a.	a - x.	$k.10^5$	(t = 0)
.04N.	45	21.31	21.14	7.8	
	109		20.93	7.2	8.0
	209		20.68	6.2	

TETRAMETHYLETHYLENEDIAMINE.

Concentrations used:- Similar to Trimethylamine.
Normal Constant.....................32.

CALCIUM CHLORIDE.

Conc.	t.	a.	a - x.	$k.10^5$	(t = 0)
N.	34	9.80	8.55	173	
	518		3.60	84	173
	617		2.85	87	

CONDUCTIVITY DATA.

Conductivity of the Formaldehyde used.

For all the experiments - Temperature = 25°C.
Cell Constant = .2187.

All the bridge wire readings,- x -, are the corrected values.

Normality of HCHO.	Resistance in Ohms.	x in cms.	$\frac{x}{100-x}$	Conductivity.
1.0	1000	10.93	.1223	2.68×10^{-5}
	2000	20.20	.2531	2.77×10^{-5}
	3000	27.8	.3850	2.81×10^{-5}
	6000	44.0	.7857	2.86×10^{-5}
	10000	57.1	1.331	2.91×10^{-5}
			Average,	2.81×10^{-5}
.5	2000	15.20	.1793	1.96×10^{-5}
	4000	27.25	.3746	2.05×10^{-5}
	6000	36.64	.5783	2.11×10^{-5}
	10000	50.30	1.012	2.21×10^{-5}
			Average,	2.08×10^{-5}
.1	5000	14.9	.1751	7.66×10^{-6}
	7000	20.9	.2642	8.25×10^{-6}
	10000	30.2	.4327	9.46×10^{-6}
			Average,	8.46×10^{-6}
.05	7000	20.2	.2531	7.91×10^{-6}
	11000	27.1	.3717	7.39×10^{-6}
			Average,	7.65×10^{-6}
.025	10000	23.8	.3123	6.83×10^{-6}

The conductivity of the formaldehyde is, therefore, negligible.

Conductivity of Sodium Hydroxide.

Normality of NaOH.	Resistance in Ohms.	x in cms.	$\frac{x}{100-x}$	Conductivity.
.1	5	33.25	.4981	2.18×10^{-2}
	10	50.00	1.0000	2.19×10^{-2}
	15	59.85	1.491	2.17×10^{-2}
			Average,	2.18×10^{-2}
.05	5	20.60	.2595	1.14×10^{-2}
	10	34.14	.5185	1.13×10^{-2}
	15	43.81	.7794	1.14×10^{-2}
	20	51.06	1.045	1.14×10^{-2}
	25	56.56	1.301	1.14×10^{-2}
			Average,	1.14×10^{-2}
.025	10	21.10	.2674	5.85×10^{-3}
	20	34.86	.5348	5.85×10^{-3}
	30	44.66	.8066	5.88×10^{-3}
	40	51.88	1.078	5.89×10^{-3}
			Average,	5.87×10^{-3}

Conductivity of Sodium Hydroxide + Formaldehyde.

Normality		Resistance in Ohms.	x in cms.	$\frac{x}{100-x}$	Conductivity.
NaOH.	HCHO.				
.1	.1	5	28.70	.4025	1.76×10^{-2}
		10	45.06	.8197	1.79×10^{-2}
		15	54.80	1.212	1.77×10^{-2}
				Average,	$1.77\ 10^{-2}$
.05	.05	5	18.46	.2262	9.90×10^{-3}
		10	31.22	.4537	9.92×10^{-3}
		20	47.73	.9130	9.99×10^{-3}
		30	57.78	1.369	9.98×10^{-3}
				Average,	9.95×10^{-3}
.025	.025	5	10.78	.1211	5.30×10^{-3}
		10	19.80	.2469	5.40×10^{-3}
		20	33.08	.4948	5.41×10^{-3}
		30	42.69	.7448	5.43×10^{-3}
		40	49.90	.9960	5.45×10^{-3}
		50	55.43	1.243	5.44×10^{-3}
				Average,	5.40×10^{-3}

Conductivity of Sodium Hydroxide + Formaldehyde.

Normality NaOH.	Normality HCHO.	Resistance in Ohms.	x in cms.	$\frac{x}{100-x}$	Conductivity.
.1	.5	5	20.16	.2524	1.10×10^{-2}
		10	33.60	.5060	1.11×10^{-2}
		15	43.27	.7626	1.11×10^{-2}
		20	50.47	1.019	1.11×10^{-2}
		25	55.97	1.273	1.11×10^{-2}
				Average,	1.11×10^{-2}
.05	.5	5	11.22	.1263	5.53×10^{-3}
		10	20.55	.2586	5.66×10^{-3}
		20	34.11	.5175	5.66×10^{-3}
		30	43.85	.7811	5.70×10^{-3}
		40	51.10	1.045	5.71×10^{-3}
		50	56.64	1.306	5.71×10^{-3}
				Average,	5.66×10^{-3}
.025	.5	5	5.90	.0627	2.74×10^{-3}
		10	11.50	.1299	2.84×10^{-3}
		20	21.00	.2658	2.91×10^{-3}
		30	28.57	.4000	2.92×10^{-3}
		40	34.77	.5332	2.98×10^{-3}
		50	40.10	.6695	2.93×10^{-3}
		80	51.80	1.075	2.94×10^{-3}
		100	57.26	1.339	2.93×10^{-3}
				Average,	2.93×10^{-3}

Conductivity of Barium Hydroxide.

Normality of $Ba(OH)_2$	Resistance in Ohms.	x in cms.	$\frac{x}{100-x}$	Conductivity.
.1	5	31.60	.4620	2.02×10^{-2}
	10	48.18	.9298	2.03×10^{-2}
	15	58.13	1.389	2.03×10^{-2}
			Average,	2.03×10^{-2}
.05	5	19.80	.2469	1.08×10^{-2}
	10	33.08	.4942	1.08×10^{-2}
	15	42.64	.7435	1.08×10^{-2}
	20	49.85	.9940	1.09×10^{-2}
	25	55.48	1.246	1.09×10^{-2}
			Average,	1.08×10^{-2}
.025	5	11.36	.1282	5.61×10^{-3}
	10	20.70	.2610	5.71×10^{-3}
	20	34.32	.5225	5.72×10^{-3}
	30	44.07	.7878	5.74×10^{-3}
	40	51.26	1.051	5.75×10^{-3}
	50	56.75	1.312	5.74×10^{-3}
			Average,	5.73×10^{-3}

Conductivity of Barium Hydroxide + Formaldehyde.

Normality		Resistance in Ohms.	x in cms.	$\frac{x}{100-x}$	Conductivity.
Base.	HCHO.				
.1	.1	5	27.25	.3746	1.64×10^{-2}
		10	42.98	.7541	1.65×10^{-2}
		15	53.04	1.130	1.65×10^{-2}
				Average,	1.65×10^{-2}
.05	.05	5	17.70	.2151	9.41×10^{-3}
		10	30.18	.4322	9.45×10^{-3}
		15	39.40	.6502	9.48×10^{-3}
		20	46.52	.8699	9.52×10^{-3}
		25	52.05	1.086	9.50×10^{-3}
		30	56.57	1.302	9.49×10^{-3}
				Average,	9.48×10^{-3}
.025	.025	5	10.53	.1177	5.15×10^{-3}
		10	19.30	.2392	5.23×10^{-3}
		20	32.42	.4797	5.25×10^{-3}
		30	41.90	.7212	5.26×10^{-3}
		40	49.10	.9646	5.27×10^{-3}
		50	54.67	1.206	5.27×10^{-3}
				Average,	5.24×10^{-3}

Normality		Resistance in Ohms.	x in cms.	$\frac{x}{100-x}$	Conductivity.
Base.	HCHO.				
.1	.5	5	19.40	.2407	1.05×10^{-2}
		10	32.30	.4771	1.04×10^{-2}
		20	48.90	.9570	1.05×10^{-2}
		30	58.90	1.433	1.05×10^{-2}
				Average,	1.05×10^{-2}
.05	.5	5	11.20	.1261	5.52×10^{-3}
		10	20.20	.2531	5.55×10^{-3}
		20	33.50	.5038	5.51×10^{-3}
		30	43.10	.7575	5.52×10^{-3}
		40	50.30	1.012	5.53×10^{-3}
		50	55.76	1.260	5.51×10^{-3}
				Average,	5.52×10^{-3}
.025	.5	5	6.25	.0666	2.91×10^{-3}
		10	11.75	.1337	2.93×10^{-3}
		20	21.10	.2674	2.93×10^{-3}
		30	28.60	.4006	2.92×10^{-3}
		40	34.74	.5325	2.91×10^{-3}
		50	40.00	.6667	2.92×10^{-3}
		60	44.46	.8004	2.92×10^{-3}
		70	48.30	.9342	2.92×10^{-3}
		80	51.65	1.068	2.92×10^{-3}
		100	57.10	1.331	2.91×10^{-3}
				Average,	2.92×10^{-3}

POLYMOLECULAR CHEMICAL REACTIONS.

POLYMOLECULAR CHEMICAL REACTIONS.

Polymolecular chemical reactions are of two types. The first class consists of these in which one molecule of each of n different substances, all originally present in the same concentrations, is necessary and sufficient for the occurrence of the change. The differential equation assumes the form-

$$dC/dt = k.C.C.C.C.\ldots\ldots\ldots\ldots(n \text{ times})$$
$$= k.C^n \qquad (1)$$

(All concentrations in this section may be taken as measured in gram molecules per litre.)

The other class is much more general, and in-cludes those reactions in which the n molecules, actually taking part in the change, are not all dif-ferent. If m_1 molecules of substance A, reacting with initial concentration C_1, disappear for every m_2 molecules of substance B,- of original concentration C_2-, used up, and so on

$$dC/dt = k.C_1C_1C_1C_1\ldots\ldots C_2C_2C_2\ldots\ldots C_3C_3\ldots\ldots$$
$$= k.C_1^{m_1}C_2^{m_2}C_3^{m_3}\ldots\ldots \qquad (2)$$

where $m_1 + m_2 + m_3 + \ldots = n$.

This equation can be put in a more useful form. If several substances A,B,C,...with initial con-centrations a,b,c,...take part in a simple reaction, undisturbed by any simultaneous or secondary changes, and if l,m,n,...are the number of molecules of A,B,C,. which/

which must react simultaneously before the change considered can take place, then, where x would be the actual fall in concentration in time t, of a substance of which only one molecule was necessary for the progress of the reaction,

$$dx/dt = k(a - lx)^{l}(b - mx)^{m}(c - nx)^{n}\ldots \qquad (3)$$

the number of factors being equal to the number of different substances taking part in the reaction. If any substances which do not react, are present, the corresponding factor has the exponent zero, and is thus unity, e.g. $(c - 0x)^0 = c^0 = 1$. A similar equation has been given by Wegscheider,[1] in a paper on "The most general form of chemico-kinetic equations for homogeneous systems".

From this general equation can be deduced all the ordinary monomolecular, bimolecular, etc. velocity of reaction formulae. For example, when two different substances, both initially present in the same concentration, react, and only one molecule of each takes part in the change, then, substituting in the equation $a = b$, and $l = m =$ unity.

$$dx/dt = k.(a - x)^2 \qquad (4)$$

This is the equation usually given.

Similarly, when three substances, originally present in different concentrations, take part in a reaction/

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1) Z. physikal. Chem.,(1900), 35, 513.

reaction, only one molecule of each being necessary for the occurrence of the change.

$$dx/dt = k.(a - x)(b - x)(c - x) \quad (5)$$

Reactions such as these present no difficulty. Trouble has, however, frequently arisen when differential equations have been required for reactions in which two or more molecules of at least one of the substances present are necessary for the progress of the change, i.e. when one or more of the quantities l, m, n, in equation (3) is greater than unity. Applying the general equation to such actions formulae of the following types are obtained.

Bimolecular:-

When a change takes place involving the interaction of two molecules of the sole reactant present, the equation (3) reduces to a single term, and, if a be the original concentration of this substance, then, since $l = 2$,

$$dx/dt = k.(a - 2x)^2 \quad (6)$$

Termolecular:-

When the change involves one substance only, the equation takes the form,

$$dx/dt = k.(a - 3x)^3 \quad (7)$$

but when two molecular species A and B take part,- their initial concentrations being a and b respectively,- and two molecules of B react with one of A,

$$dx/dt = k.(a - x)(b - 2x)^2 \quad (8)$$

In a formula such as

$$dx/dt = k.(a - 3x)^3 \qquad (9)$$

where a is the total initial concentration of the reactant, of which three molecules take part in the change, and x is the reduction in concentration in time t, due to each molecule reacting,- it is quite allowable, if absolute values of the velocity constant are not required, to make the substitution $x_1 = 3x$, whence

$$dx_1/dt = k_1(a - x_1)^3 \qquad (10)$$

The constants obtained from equation (9) are a constant multiple of these given by formula (10). This can be seen by comparing the integrated forms which are -

$$k = \frac{1}{6t}\left\{\frac{1}{(a - 3x)^2} - \frac{1}{a^2}\right\}$$

$$k_1 = \frac{1}{2t}\left\{\frac{1}{(a - x_1)^2} - \frac{1}{a^2}\right\}$$

$$\therefore\ k_1 = 3k.$$

It would not, however, be justifiable to use the equation

$$dx/dt = k_2(a - x)^3 \qquad (11)$$

where a and x have the same significance as in (9). This also can be readily proved by comparing the integrated forms. On integration (9) gives the following expression for k.

$$k = \frac{1}{6t}\left\{\frac{1}{(a - 3x)^2} - \frac{1}{a^2}\right\}$$

whence - $$k = x/2a^2t\left\{\frac{2a - 3x}{(a - 3x)^2}\right\}$$

Similarly (11) gives -

$$k_2 = \frac{1}{2t}\left\{\frac{1}{(a - x)^2} - \frac{1}{a^2}\right\}$$

$$k_2 = x/2a^2t\left\{\frac{2a - x}{(a - x)^2}\right\}$$

The values of k and k_2 can only be equal in the very special cases when $x = 2.215a$ or $0.4515a$, and the one is a constant multiple of the other, $(k = pk_2)$, only when the values of a and x satisfy the equation

$$(9p - 3)x^3 - (24p - 8)ax^2 + (13p - 7)a^2x - (2p - 2)a^3 = 0$$

In general, therefore, the two forms do not give the same constants, or even the one set a constant multiple of the other.

Several authors have virtually made this mistake of neglecting the coefficients of x. For instance, Noyes and Cottle[1) employ the formula

$$dx/dt = k.(a - x)(b - x)^2 \qquad (12)$$

where a and b are the initial concentrations of substances A and B, of which one molecule of the first and two of the second take part in the reaction. The concentration of B falls at twice the rate of that of A, but the equation chosen does not show this.

This mistake has been so common that further proof of the insufficiency of the formulae used will be given. The/

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1) Z. physikal. Chem., (1898), 27, 579.

The reaction studied by Noyes and Cottle[1)] can be represented by the equation

$$2CH_3COOAg + HCOONa = 2Ag + CO_2 + CH_3COOH + CH_3COONa$$

In their calculations they employ formula (12), where a and b are the initial concentrations of sodium formate and silver acetate respectively, and x is the measured fall in concentration of the latter substance. Considered from the kinetic standpoint their equation is readily seen to be incorrect.

If the silver acetate be taken in excess, then, when the fall in its concentration is twice the original concentration of the sodium formate, the latter substance will disappear altogether, and the velocity of reaction will be zero.

i.e. $dx/dt = 0$, when $x = 2a$.

Noyes and Cottle's equation states that the reaction will finish when $x = a$. The formula which they should have used evidently is

$$dx/dt = k.(a - x/2)(b - x)^2 \qquad (13)$$

This is identical in form with equation (8), as can be seen by making the substitution $y = x/2$, when it becomes

$$dy/dt = k_1(a - y)(b - 2y)^2$$

Similar formulae to these given can be deduced from the general equation, for reactions of any order. The use/

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1) Z. physikal. Chem., (1898), 27, 579.

The use of erroneous formulae by several workers is possibly due to their having accepted without question these given by Ostwald[1], and integrated by Fuhrmann[2].

The form of the equations, which should be used in any particular case, having been settled, the evidence for the existence of termolecular reactions, in particular, will now be reviewed.

It has often been found that in place of an expected reaction of the third order, one of lower order has been shown to hold. Mellor[3] explains this well in the following words, "Reactions of higher order than the second are not very common. This is easily understood if we assume that bimolecular reactions are caused by the collision of two molecules, termolecular reactions by the collision of three molecules, etc. The probability of a simultaneous collision between three molecules is very much less than between two molecules, and the greater the number of molecules taking part in a given trans--formation, the more likely is the reaction to proceed by some other path than by the simultaneous collision of the reacting molecules." In Nernst's[4] opinion, the velocity of polymolecular reactions can be appreciable only under/

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[1] Lehrbuch d. allgemeinen Chemie, (1887), 2, 615-634.
[2] Z. physikal. Chem., (1889), 4, 89.
[3] Chemical Statics and Dynamics, (1904), 53.
[4] Nernst, Theoretical Chemistry, (1923), 651.

under quite exceptional conditions, and hence most apparently polymolecular reactions really take place by means of simpler (uni-, bi-, and very rarely tri-molecular) ones which occur successively.

The work of Knoblauch[1)] on the velocity of saponification of esters of polybasic acids affords an excellent example of this. If the radicle of a dibasic acid be represented by R'', its ethyl ester is saponified by caustic soda according to the equation

$$R''(C_2H_5)_2 + 2NaOH = R''Na_2 + 2C_2H_5OH.$$

This, however, does not indicate what appears to be the true course of the reaction. The change is not termolecular, but occurs in two stages,

$$1)\ R''(C_2H_5)_2 + NaOH = R''(C_2H_5)Na + C_2H_5OH$$

$$2)\ R''(C_2H_5)Na + NaOH = R''Na_2 + C_2H_5OH$$

and consists, therefore, of two consecutive bimolecular reactions.

The saponification of methyl acetate by calcium hydroxide, instead of being a reaction of the third order,

$$2CH_3COOCH_3 + Ca(OH)_2 = (CH_3COO)_2Ca + 2CH_3OH$$

probably proceeds according to the following equations,

$$CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOCH_3.H_2O \quad \text{(Fast)}$$

$$CH_3COOCH_3.H_2O + OH' = CH_3COO' + CH_3OH \quad \text{(Slow)}$$

and should/

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1) Z. physikal. Chem., (1898), 26, 96.

should, therefore, give a bimolecular constant.

It is not surprising then that the number of changes which are believed to be termolecular is very small. In fact it is very doubtful if there is a single well authenticated example of such a reaction in the literature. A number of the cases usually quoted are given in the following list.

a) Polymerisation of cyanic acid.(1)

b) Decomposition of potassium hypoiodite.(2)

c) Action of stannous chloride upon ferric chloride.(3)

d) Action of silver acetate upon sodium formate.(4)

e) Union of hydrogen and oxygen.(5)

f) Action of sodium hydroxide upon benzaldehyde.(6)

g) Oxidation of sulphur dioxide.(7)

h) Union of carbon monoxide and oxygen.(8)

A few of these will now be considered, and the evidence which has been advanced in favour of the existence of termolecular reactions reviewed.

Schwicker(2) has studied the transformation of potassium hypoiodite into iodate, and concludes that it is a reaction of the third order. This/

1) J.H. van't Hoff, Études, (1884), 90.
2) A. Schwicker, Z. physikal. Chem.,(1895), <u>16</u>, 303.
3) Noyes, Z. physikal. Chem.,(1895), <u>16</u>, 546;
(1896), <u>21</u>, 16.
4) Noyes & Cottle, Z. physikal. Chem., (1898), <u>27</u>, 579.
5) Bodenstein, Z. physikal. Chem., (1899), <u>29</u>, 665.
6) Pomeranz, Monatsh., (1900), <u>21</u>, 389.
7) Bodländer & Köppen, Z. Elektrochem.,(1903), <u>9</u>, 559.
8) Z. physikal. Chem., (1903), <u>44</u>, 385.

This change is generally represented by the equation

$$3KIO = KIO_3 + 2KI.$$

and should accordingly give a termolecular constant. He employs the following formula, which is correct,

$$dx/dt = k.(A - x)^3.$$

where

$\left\{\begin{array}{l}\underline{A} \text{ is the initial concentration of the hypoiodite, and} \\ \underline{x} \text{ is the reduction in concentration during time } \underline{t}.\end{array}\right.$

When there is an excess of iodine present, the integrated expression gives a constant value, but when the potassium hydroxide is in excess a very good bimolecular constant is obtained. What the course of the reaction is, and what is the equation which represents it, are left unanswered. Such results can hardly be taken as evidence for the existence of termolecular reactions. Moreover, Taylor 1) considers that Schwicker's results are not altogether satisfactory, as he neglects the effect of the potassium iodide in his "iodine" solution. That the rate of formation of iodate is largely dependent on the concentration of the iodide is shown by Foerster and Gyr 2) in a paper on " The action of iodine on alkalis." These observations are extended by Forster 3), and it seems reasonable to conclude that, with such evidence against his work, Schwicker's deductions cannot be accepted.

1) Chem. News, (1897), 76, 17.
2) Z. Elektrochem., (1903), 9, 1.
3) J. Physical Chem., (1903), 7, 640.

The reduction of silver acetate by sodium formate is, according to Noyes and Cottle 1), a ter-molecular process, and the equation as usually written is

$$2CH_3COOAg + HCOONa = 2Ag + CO_2 + CH_3COOH + CH_3COONa. \qquad (14)$$

These workers use the formula

$$dx/dt = k.(a - x)(b - x)^2 \qquad (15)$$

where
$\underline{a}$ = total initial concentration of $HCOONa$.
$\underline{b}$ = total initial concentration of CH_3COOAg.
$\underline{x}$ = fall in concentration of CH_3COOAg in time $\underline{t}$.

This has already been shown to be quite in error, and thus the constants which they obtain are valueless for proving the occurrence of reactions of the third order.

When the data given are substituted in the correct equation

$$dx/dt = k.(a - x)(b - 2x)^2. \qquad (16)$$

where
$\underline{a}$ = total initial concentration of $HCOONa$.
$\underline{b}$ = total initial concentration of CH_3COOAg.
$\underline{x}$ = fall in concentration of $HCOONa$ in time $\underline{t}$.

constants are not obtained, which proves that the reaction is not simply a termolecular change.
(In the tables on the following page (B - x) is the value given by Noyes and Cottle for the concentration of silver acetate remaining at the time indicated.)

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1) Z. physikal. Chem., (1898), 27, 579.

A = conc. HCOONa.	B = conc. CH_3COOAg	t.	B - x.	k_3(N.&C)	$k_3$cor.
.100	.100	2	.06694	30.8	27.3
		4	.05334	31.3	25.6
		6	.04684	29.6	22.9
		9	.03784	33.3	23.2
		14	.03235	30.6	19.6
.050	.100	2	.08103	30.0	26.2
		4	.07180	30.2	23.5
		7	.06395	31.2	20.6
		11	.05920	29.7	16.9
		16	.05625	28.0	13.5
.025	.050	10	.03766	37.3	30.5
		25	.03136	38.6	24.7
		45	.02840	37.3	18.7
		80	.02653	34.4	12.8

Under k_3(N.& C.) are given Noyes and Cottle's constants, under $k_3$cor. those calculated from formula (16).

Brönsted [1], accepting their figures, has tried to explain the fall in the constants with rise in total concentration of the reactants, and finds some "complicated relationship" which he cannot explain. He suggests that the reaction may not be of the third order, and shows, in the following manner, how a bimolecular reaction might lead to a formula of a termolecular nature.

If we suppose that the reaction really takes place between silver ions, and undissociated silver formate, and is bimolecular,

$$dx/dt = k.(Ag^{\cdot})(\text{Undissoc.}HCOOAg) \qquad (17)$$

Now consider the equilibrium

$$HCOOAg \rightleftharpoons HCOO' + Ag^{\cdot}$$

whence

$$(Ag^{\cdot})(HCOO') = \phi(v)(HCOOAg) \qquad (18)$$

In dilute/

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[1] Z. physikal. Chem., (1922), <u>102</u>, 193.

In dilute solution $\phi(v)$ - a term expressing the effect of dilution on the ionisation of the salt - will not alter appreciably. Therefore, substituting in equation (17),

$$dx/dt = k_1(Ag^{\cdot})^2(HCOO'). \qquad (19)$$

which is identical with the equation for a reaction of the third order on which Noyes and Cottle based their work, and which is derived as follows:-
Equation (14) reduces to

$$2Ag^{\cdot} + HCOO' = 2Ag + CO_2 + H^{\cdot}$$

whence

$$dx/dt = k.(Ag^{\cdot})^2(HCOO').$$

Brönsted, then, shows that even though Noyes and Cottle had obtained constants, using a correct formula, their results would not necessarily have proved the reaction to be termolecular.

Noyes and Cottle's experiments, therefore, give no evidence whatever in favour of the existence of reactions of the third order.

Pomeranz 1) has studied the action of sodium hydroxide on benzaldehyde, and believes this to be a termolecular change. The formulae he uses are quite correct, and the constants obtained satisfactory. However, certain of his arguments detract considerably from the value of his paper. For example, he finds that the velocity constant increases with increasing initial concentration/

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1) Monatsh., (1900), 21, 389.

concentration of the reactants, and from this fact, without further proof of any kind, makes the statement that only the undissociated caustic soda molecules participate in the reaction. His results, as they stand, although apparently better than those of many other workers, cannot be accepted as good evidence for the type of reaction under consideration.

Kühl[1] has studied the kinetics of the reaction between carbon monoxide and oxygen, which, as far as the final change is concerned, proceeds according to the equation

$$2CO + O_2 = 2CO_2$$

He finds that the reaction appears in general to be of the third order, but that the results obtained are irregular. The equation used when the gases are not taken in equivalent amounts is correct, but his formula for the velocity of reaction when equivalent quantities are originally present is incorrect. Reactions between gases are specially liable to disturbing influences, and his experiments have been no exceptions. Whatever be the meaning of his results, they cannot be taken as good evidence for the existence of termolecular reactions.

In a paper on " The rate of formation of sulphur trioxide in presence of platinum", Bodländer and Köppen[2] employ the correct formulae. Their results are, however, difficult to interpret. A change in the conditions of

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1) Z. physikal. Chem., (1903), <u>44</u>, 385.
2) Z. Elektrochem., (1903), <u>9</u>, 559.

the experiment makes a great difference in the apparent order of the reaction, and although a number of the results are in fair agreement with the requirements of the equation for a reaction of the third order, the research as a whole cannot be said to give much support to the existence of changes of the kind considered.

Bodenstein 1) has studied the combination of hydrogen and oxygen to give water, and, according to the ordinary equation

$$2H_2 + O_2 = 2H_2O,$$

it would be expected to obey the law for a reaction of the third order. Little fault can be found with the formulae he employs for the calculation of his constants; they only differ from the correct equations by a constant ~~term~~ factor. The results obtained are, however, very unsatisfactory, and he confesses that he cannot explain the irregularities. This, being a gas reaction, is liable to disturbing influences such as the catalytic effect of the walls of the containing vessel, but, apart from this, the reaction very probably takes place by a series of changes, each of lower order than the third. His research cannot be said to have strengthened the evidence for the occurrence of termolecular processes.

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1) Gasreaktionen in der chemischen Kinetik, V, Z. physikal. Chem., (1899), 29, 676.

One of the standard examples of a reaction of the third order is that originally investigated by Noyes[1]. He studied the action of stannous chloride on ferric chloride, for which the following equation is usually given

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

In the theoretical section of his paper he points out that if the number of substances taking part determines the velocity with which the reaction proceeds, then the differential equation takes the form

$$dx/dt = C_2(A - x)(B - x)$$

If, on the other hand, the number of molecules reacting is the deciding factor, then, in his opinion, the following expresses the rate

$$dx/dt = C_3(A - x)(B - x)^2$$

where in both formulae

$$\begin{cases} \underline{A} = \text{total initial concentration of } SnCl_2, \\ \underline{B} = \text{total initial concentration of } FeCl_3, \\ \underline{x} = \text{fall in concentration of } SnCl_2 \text{ in time } \underline{t}. \end{cases}$$

When equivalent amounts of the stannous and ferric chlorides are taken, he finds the constants of the third order bad, but much better than those of the second. When the concentrations of the reactants are not equal, satisfactory constants are never obtained. All that can be said for those of the third order/

[1] Z. physikal. Chem., (1895), 16, 546.

order is that they are much less variable than those of the second. From evidence based largely on these "constants" he concludes that the reaction, although disturbed, is undoubtedly a termolecular process.

Apart from the unsatisfactory nature of the "constants", it is evident that he has employed an incorrect termolecular formula. His results, therefore, even though they could be accepted as sufficiently constant, cannot be taken as evidence in favour of the reaction being of the third order.

In fact other investigators consider the change to be bimolecular. Kahlenberg 1) gives figures which he believes are accurate enough to prove this. His results, however, are not convincing.

Kortright 2) takes into account the fact that stannous and ferric chlorides are hydrolysed in solution, and recalculates Kahlenberg's results, substituting in each case the concentration of unhydrolysed salt for the total concentration of the chloride. By this method he obtains exceedingly good bimolecular constants.

Noyes 3) has replied to Kortright, saying that the latter's explanation is valueless, as results obtained by Goodwin 4) show that the hydrolysis of ferric chloride to ferric hydroxide/

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1) J. Amer. Chem. Soc., (1894), <u>16</u>, 314.
2) Amer. Chem. Jour., (1895), <u>17</u>, 116.
3) Z. physikal. Chem., (1896), <u>21</u>, 16.
4) Z. physikal. Chem., (1896), <u>21</u>, 1.

hydroxide can occur only to a very small extent - less than that required by the explanation given.

Whatever be the truth with regard to the points raised in these papers, it is quite obvious that there is as yet no evidence to prove that this reaction is termolecular. In fact the balance is in favour of a lower order, complicated in some unexplained manner.

In all the examples given the stoichiometric equation would lead one to expect a reaction of the third order, but it is important to distinguish between such an equation and the equation or equations which truly represent the course of the change taking place. The evidence in favour of termolecular processes has, in nearly all the cases quoted, been of a very doubtful nature, and is certainly not of such a kind as can be accepted as proof of the occurrence of such changes. From kinetic and other points of view there is much reason to believe that the changes take place by a series of reactions of the second order, and that the higher polymolecular reactions quoted in literature are equally simple in their mechanism. Rice's 1) statement with respect to unimolecular reactions sums up the case for those of the third order: " Amongst the great number of measurements of velocity of chemical reactions there are none in which we are reasonably sure that a unimolecular reaction is occurring".

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1) Taylor - A Treatise on Physical Chemistry, (1924), Vol.2, p.868.