XLIV.—*The Reaction between Hydroxylamine and Ferric Chloride.*

By Alec Duncan Mitchell.

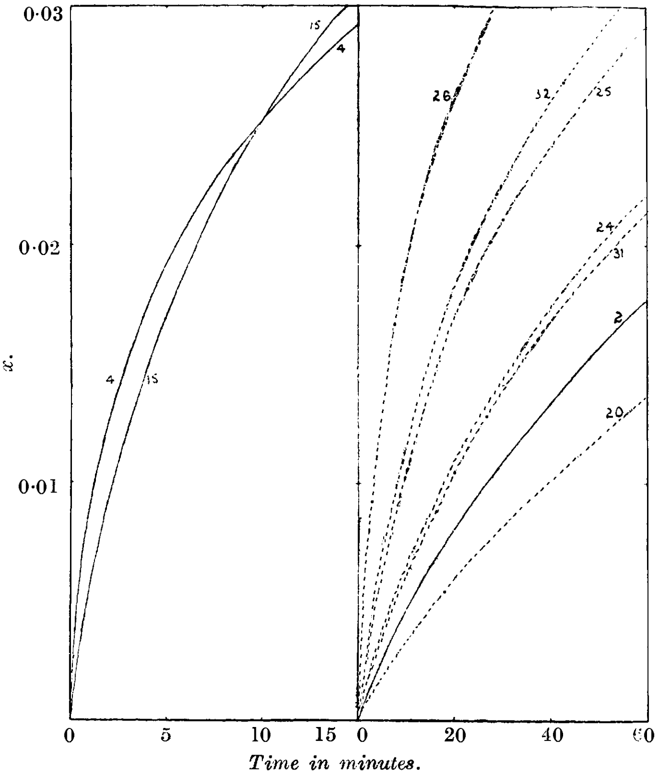
Hydroxylamine is a compound of great interest from several points of view. Many years ago Haber showed (*Ber.*, 1896, **29**, 2444) that it would oxidise ferrous salts in alkaline solution or suspension, and reduce ferric salts in acid solution, and he suggested that its structure in the two cases might be represented as $H_3N\colon O$ and $H_2N{\cdot}OH$ respectively. The existence of such dynamic isomerides would account for the above behaviour, which is typical of many of the reactions of hydroxylamine, and, with the object of seeking a further basis for this hypothesis, the author has carried out several kinetic studies, since similar investigations have afforded such evidence in other cases (Mitchell, J., 1923, **123**, 629, 2241).

The reactions of hydroxylamine are all very complicated, and, up to the present, only one, the subject of this communication, has been interpreted. It may be stated at once that, possibly because the acidic solutions involved may exclude one isomeride, the results have no bearing on the main problem, but they are of interest in other respects.

A kinetic study of the reactions of hydroxylamine appeared desirable in that no such examination has hitherto been made. A survey of the literature discloses more than twenty reactions in which the ultimate products have been studied, but the mechanism underlying their formation has usually been ignored. There are two partial exceptions to this statement: (1) Raschig ("Schwefel- und Stickstoff-Studien," 1924) studied the stoicheiometrical ratios obtaining at various stages in the course of certain reactions, but did not investigate them kinetically; and (2) Brönsted (*Z. physikal. Chem.*, 1922, **102**, 187) made a rough colorimetric estimate of the effect of a saline solution on the reaction now discussed, and, from the apparent absence of appreciable "salt effect," concluded that reaction takes place between the metallic ion and undissociated hydroxylamine molecule to form a "critical complex." As will be seen later, however, the more accurate method used here indicates a definite negative salt effect (p. 347).

There seemed to be two difficulties in the way of the proposed investigations: (1) few of the reactions proceed quantitatively in one direction, the majority giving varying proportions of by-products, and (2) hydroxylamine reacts more or less readily with most of the reagents which might normally be employed in the estimation of the second reactant or the products. The second difficulty has been obviated in the present instance by analytical methods which are described in the experimental portion of this communication. The first difficulty has been minimised by choosing reactions, such as that under discussion, which appear to give but little by-product. In the present case, the reaction is quantitative under the conditions laid down by Raschig (*Annalen*, 1887, **241**, 190)—considerable excess of ferric salt and of sulphuric acid, and at least five minutes' boiling. These conditions could not, for various reasons, be applied in the present research, but it is believed that the necessary departures from them involve only slight errors. There is no doubt that the difficulties which had to be overcome by Raschig were the slowness of the reaction in its later stages and the possible persistence of an intermediate product. The former difficulty is immaterial in an investigation such as this, and the latter is only of importance in so far as it affects analysis, but the method used is believed to eliminate this effect (p. 346). A consideration of the work of Bray (*J. Amer. Chem. Soc.*, 1919, **41**, 1363) in conjunction with that of Kurtenacker and Neusser (*Z. anorg. Chem.*, 1923, **131**, 27) shows that, using only a bare excess of ferric salt, reaction is incomplete simply because it becomes extremely slow, and that, using neutral or very feebly acidic solutions, there is slight formation of elementary nitrogen, corresponding to 4%, at most, of the hydroxylamine. Apart from this, these authors find no evidence of side-reactions, and it would therefore appear that the departures from the prescribed conditions do not materially affect the present research. The author's experience confirms the production of traces of nitrogen in the least acidic solutions, and also indicates that, under the conditions which are imposed upon this research—restrictions which often necessarily obtain in kinetic studies—traces of higher oxides of nitrogen are produced (p. 346).

FIG. 1.



Mechanism of the Reaction.

The complete reaction under ideal conditions is represented by

$$4Fe^{\cdots} + 2NH_3OH^{\cdot} = 4Fe^{\cdot\cdot} + 6H^{\cdot} + N_2O + H_2O$$

and the molar concentrations of the first four species will be represented by a, $b/2$, f, and h respectively. It will be seen that, if the suffix 0 represent these at zero-time, and the suffix t at any specified time corresponding to the reduction of x moles of ferric iron, then $a_t = a_0 - x$, $b_t = b_o - x$, $f_t = f_0 + x$, and $h_t = h_0 + 3x/2$.

A few experiments using ferric chloride and hydroxylamine hydrochloride led to no conclusion as to the order of the reaction. The initial velocity was enormous, but was damped down so rapidly that, unless a reaction of about the tenth order was assumed, one had to ascribe repressing effects to one or more of the products of reaction. Even when the velocity became of a lower order, a reduction of, say, 5%, in the concentrations of ferric iron and hydroxylamine caused the velocity to be reduced to one-half or less (see Expt. 1 as an example). (The reduction of cupric salts by hydroxylamine in the presence of acetic acid and sodium acetate is found to be similar in this respect.)

The initial addition of hydrochloric acid produced much slower reactions, but the damping was still so marked that a second product of reaction was suspected of a repressing effect (see Fig. 1, Expt. 4). Initial addition of ferrous salts also produced a great depression in velocity whether hydrochloric acid had been added or not. (The effects of equi-molar additions of hydrochloric acid or ferrous salts were not quite the same.) When both hydrochloric acid and ferrous salts were present in fair concentration, the reaction was closely termolecular—bimolecular with regard to ferric iron and unimolecular with respect to hydroxylamine. The termolecular velocity coefficient fell off slightly, but this was provisionally attributed to the progressive accumulation of ferrous and hydrogen ions, as reaction in the presence of a large excess of both was too slow for a more rigid test to be practicable. No other type of ordinary velocity coefficient gave any approach to constancy.*

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* In this connexion may be mentioned an interesting instance of the danger of relying on initial velocities from a few isolated experiments as a clue to the order of reaction : in a few runs with initial hydrochloric acid and hydroxylamine kept constant, the apparent initial velocity (that based on the gross change before the first titration) was roughly proportional to the initial concentration of ferric chloride, which was varied, and the erroneous deduction was drawn that this was involved to only the first order. The explanation is due to the fact that, as will be seen later, the velocity in these experiments is inversely proportional to the concentration of ferrous iron, so that $\delta x \propto a^2/f$; since f increases from zero to δx in the small interval concerned, its mean concentration is $\delta x/2$, so that $\delta x \propto a^2/\delta x/2$ as an approximation, or $(\delta x)^2 \propto a^2$ or $\delta x \propto a$—thus accounting for the erroneous conclusion. Strictly, one is dealing with an integral summation starting with an infinite velocity for an infinitely short time, but actually the velocity is of a measurable order almost instantly, so that the approximation involved here is sufficiently near the truth to account for the observed facts.

The effects of the products of the reaction in repressing it indicated an equilibrium as an *intermediate* stage in the reaction; and it could be *only an intermediate stage* because the reaction goes to completion, forming the basis of Raschig's method for the estimation of hydroxylamine, so that the ultimate products could not reverse the reaction.

Further evidence bearing on the equilibrium was obtained when certain experiments, the early stages of which were too rapid for detailed measurement at 25°, were carried out at 15·5°. Seven experiments, of various types, all gave the temperature coefficient of 5·9 for 9·5°, which, by exponential proportion, becomes 6·5 for 10°. Just as temperature coefficients of less than unity—or negative coefficients as they would be if expressed more rationally—are interpreted as evidence of intermediate compounds (Eggert, *Z. Elektrochem.*, 1921, **27**, 455, and Skrabal, *ibid.*, 1915, **21**, 461, on the Landolt reaction, and Hasche and Patrick, *J. Amer. Chem. Soc.*, 1925, **47**, 1214, on the reaction between nitric oxide and oxygen), so this abnormally high temperature coefficient is regarded as indicating the existence of an intermediate equilibrium, which is displaced, by a rise in temperature, in a direction more favourable to reaction, this accelerating effect being superimposed upon the normal temperature effect.

No attempt has been made to correct for incomplete ionisation of electrolytes; the corrections which have been made for salt effect (p. 349) in certain cases tend to make a rough correction of this kind, however, and serve to make experiments more comparable.

The recognised methods of treating reaction velocities fail where the indications are that the initial velocity is infinite or of a very high magnitude. It was therefore necessary to obtain expressions, even if they were empirical, which would represent the course of the reaction, before one could draw any conclusions of a quantitative nature, and subsequently a certain amount of theoretical justification was found for them. As a tentative expression the following was used :

$$\frac{dx}{dt} = k_1 \frac{(a - x)^2(b - x)}{(h + 3x/2)(f + x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)^*$$

It is here necessary for the purposes of discussion to classify experiments into four types as follows :

(I) Those having only ferric chloride and hydroxylamine hydrochloride initially.

(II) Those having additional hydrochloric acid alone initially.

(III) Those having additional ferrous iron alone initially.

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* The integrals of all the formulæ used here are very cumbersome and their calculations are tedious, so details are omitted.

(IV). Those having both additional hydrochloric acid and ferrous iron initially.

Expression (1) gave for all experiments, except those of type (I), values for k_1 which were reasonably constant in any one experiment, as is shown for two types by Expts. 5 and 18. The values showed a slight tendency to fall as a rule, and, as will be seen in the table, varied from one experiment to another in such a way as to suggest that the second power of $(h + 3x/2)$ should replace the first power. When this amended expression

$$\frac{dx}{dt} = k_2 \frac{(a - x)^2(b - x)}{(h + 3x/2)^2(f + x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is applied to the experiments the results are as shown in the same table. In this table, the values of a, b, f, and h are expressed in moles per litre and relate to initial conditions; the values of k_1 and k_2 as found from the differential determinations of velocity (see p. 347) are shown as well as those obtained by integration: the latter often obscure marked drifts towards the end of a reaction and thus are not so trustworthy in these circumstances as the differential values, although they are far less subject to experimental error. In experiments of types (I), (II), and (III), where the initial velocity is very great, the integrated values are a more trustworthy guide as to the course of the early stages of the reaction. Although k_2 shows a rise throughout every reaction, it is noteworthy that its order of magnitude is very consistent throughout the whole range of experiments, which cover a wide variety of conditions and are usually continued until over 50% of the possible reaction is completed—this extent is indicated for each experiment in the column " % completed." As it was highly improbable that this consistency was a mere coincidence, a search was made for a theoretical basis which would account for the general agreement and possibly afford a reason for the anomalies noticed.

If the hypothetical nitroxyl were produced according to the equation $2Fe^{\cdot\cdot\cdot} + NH_3OH^{\cdot} \rightleftharpoons 2Fe^{\cdot\cdot} + 3H^{\cdot} + HNO$ (and subsequently decomposed to nitrous oxide), this would be expected to play a part in the repression of the reaction, and the effect of ferrous and hydrogen ions would be more nearly in proportion to the second and third powers of their respective concentrations. As a matter of fact, the introduction into the formulæ of any function of x, giving, for example, $dx/dt = ka^2b/hfx$ or $dx/dt = ka^2b/h^2fx$, renders them quite incapable of representing the course of reaction; and the use of the second or third powers of f or h respectively is similarly useless. The absence from (2) of any term representing an intermediate compound seems to be capable of explanation as follows.

One has circumstantial evidence for assuming the formation of a complex, thus :

$$2Fe^{\cdot\cdot\cdot} + NH_3OH^{\cdot} \rightleftharpoons Fe^{\cdot\cdot} + 2H^{\cdot} + (Fe,H,NOH)^{\cdot\cdot\cdot};$$

denoting the complex by M and its concentration by m, and assuming it to decompose to nitrous oxide according to a unimolecular law, we have for the rate of accumulation of M :

$$dm/dt = k_3a^2b - k_4h^2fm - k_5m \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and for the rate of diminution of ferric iron :

$$dx/dt = k_3a^2b - k_4h^2fm = dm/dt + k_5m \quad . \quad . \quad . \quad . \quad (4)$$

(If one deals with the very early stages of reaction, it would be necessary to allow for the fact that a certain amount of hydrogen and ferrous ions is locked up in the complex M, and is therefore present as such in a concentration less by an amount m than the values $(h + 3x/2)$ and $(f + x)$; the error involved by ignoring this is small when h_0 and f_0 are finite, however, and the equations would become extremely complicated.)

After the very early stages of a reaction, m tends to keep nearly constant, owing to a compensating effect of the three reactions tending to adjust it; one would then have $dm/dt = 0$, and $dx/dt = k_5m = k_3a^2b - k_4h^2fm$. Solving for m and substituting, one has

$$dx/dt = k_3k_5a^2b/(k_4h^2f + k_5) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

When both h_0 and f_0 are zero, $dx/dt = k_3a^2b$, independently of any simplifying assumptions, and, since reaction is so rapid, it is certain that k_3 must be very large. Such a condition only obtains in the initial stages, to which expression (5) does not apply, owing to the nature of the assumptions made. The term k_4h^2f in experiments of types (II) and (III) rapidly becomes of a finite order, and in type (IV) is already of a finite order, so that, as soon as k_4h^2f becomes markedly greater than k_5, one arrives at the same expression as was obtained empirically, k_3k_5/k_4 being equal to k_2 in (2). The expressions (3) and (4) are too complicated for complete solution, so that one is unable to find whether they would account for the rise in the value of k_2 or for certain other discrepancies to be discussed later.

It is possible that reaction involves the free undissociated basic molecule: $2Fe^{\cdot\cdot\cdot} + NH_2{\cdot}OH \rightleftharpoons Fe^{\cdot\cdot} + H^{\cdot} + (NOH, Fe,H)^{\cdot\cdot\cdot}$. This mechanism would lead to an expression such as (1) but the term $(b - x)$ would have to be corrected in order to make it correspond to the free base. After the hydrogen-ion concentration reaches a value which is very early attained in experiments of types (I) and (III) and which obtains initially in the other types, this corrected term becomes approximately $(b - x)k_h/(h + 3x/2)$, k_h being the hydrolytic dissociation constant of hydroxylamine hydrochloride. An expression similar to (2) therefore results, and, as this expression is not applicable to the early stages, a decision between this possibility and that developed above cannot be made. It is believed, however, that the extremely rapid fall in the initial concentration of free basic molecules in experiments of types (I) and (III) would require an even greater fall in velocity than is actually found, so that the foregoing hypothesis is preferred.

Discussion of Results.

An apparent anomaly is exhibited by Expts. 15 and 23 in type (III), since k_1 rises at first in these cases but falls as a rule, and in this type alone k_2 appears to be zero initially. The latter fact is immaterial in view of the way in which k_2 is derived on theoretical grounds, and it cannot be expected to hold at $t = 0$. The fact that k_1 exhibited a different behaviour in these experiments from the more usual behaviour is connected with the circumstance that initial ferrous iron depresses more than initial equi-molar hydrogen ions, as is shown by the curves for Expts. 4 and 15 (Fig. 1), Expts. 22 and 23 being similar. In each case, however, as the curves show, the experiment with more ferrous iron overtakes the other as hydrogen ions accumulate during the progress of the reaction, and then one has the conditions which prevail in type (IV), where hydrogen ions depress to a greater extent than the equi-molar ferrous ions —see Expts. 17 and 18 or 13 and 14. All these peculiarities become normal when one considers the way in which $(h_0 + 3x/2)^2(f_0 + x)$ varies differently with increase in x according as h_0 or f_0 is zero or both finite, and are due ultimately to the fact that the functions of hydrogen ions and ferrous ions in repressing the reaction are different.

There still remains the interesting fact that, even after corrections have been made for salt effect (p. 349), experiments in which ferrous iron is added initially seem to give slightly lower values for k_2 with increasing amounts of ferrous iron. No satisfactory explanation has been found for this behaviour. On the other hand, both k_1 and k_2 are far more satisfactory in experiments in which there is no initial ferrous iron (type II) than in those where there is no initial acid (type III), so that the equations used appear to be more satisfactory for relatively rapid increases of ferrous iron than of hydrogen ions.

With the object of gaining further insight into the mechanism and of obtaining an estimate of the extent to which hydrogen and ferrous ions are diminished owing to the existence of the complex, six experiments were devised so as to correspond with the various conditions which might obtain in Expt. 2 after it had reached a certain stage. Initially it had $a = 0{\cdot}200$, $b/2 = 0{\cdot}100$, and the stage chosen was when 0·075 of the ferric iron had been reduced. At this stage, which was attained in 29·5 minutes, one would have $h = 0{\cdot}075 \times 3/2$ and $f = 0{\cdot}075$ if 3 and 2 atoms of hydrogen and iron respectively remained free in solution according to the stoicheiometric equation. The six experiments were chosen with the above values of a and b and with concentrations of h and f as shown :

Expt.	*h.*	*f.*						
20	0·1125	0·0750	corresponding to	$3H^{\cdot}$	and	$2Fe^{\cdot\cdot}$	remaining	free.
24	0·0750	0·0750	,, ,,	$2H^{\cdot}$	,,	$2Fe^{\cdot\cdot}$	,,	,,
25	0·0750	0·0375	,, ,,	$2H^{\cdot}$	,,	$Fe^{\cdot\cdot}$	,,	,,
26	0·0375	0·0375	,, ,,	$H^{\cdot}$	,,	$Fe^{\cdot\cdot}$	,,	,,
31	0·1125	0·0375	,, ,,	$3H^{\cdot}$	,,	$Fe^{\cdot\cdot}$	,,	,,
32	0·0375	0·0750	,, ,,	$H^{\cdot}$	,,	$2Fe^{\cdot\cdot}$	,,	,,

As can be seen from the curves * (Fig. 1), the initial velocities are slower in the case of Expt. 20, and faster in all the others, than the reaction from the corresponding point in Expt. 2, the curve in the case of this experiment being plotted with the origin corresponding to the stage concerned. This would indicate that in Expt. 2 there are fewer hydrogen and ferrous ions opposing reaction than in Expt. 20, some being locked up in the complex. On the other hand, in Expt. 2 the complex is already at the concentration imposed by the stabilising effect of the reactions affecting it, whereas, in the earliest stages of the other reactions, it has probably not attained such a condition, so that comparisons are not rigid. Passing to the general course of the curves, it would appear that the conditions in Expt. 2 are such as would be expected from the repressing effect of approximately 2·7 moles of hydrogen ion and 1·7 moles of ferrous ion, for, considering the various values of t for constant values of x (which is the correct criterion), its curve is slightly farther from that of Expt. 20 than from a compromise between those of Expts. 24 and 31 which would approximately represent 2·5 and 1·5 moles respectively ; as it is also about one-third of the way between those of Expts. 20 and 25, it would appear to correspond to 2·67 and 1·67 moles of hydrogen and ferrous ions respectively ; both situations suggest that only about one-third of the hydrogen and ferrous ions which might possibly be locked up in the complex are actually so, or that two-thirds of the total complex formed have already broken down to final products.

Although the results in the foregoing discussion leave many details

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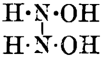
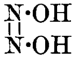
* In these curves the extent of reduction (x) is plotted against time (t) which has been reduced in accordance with the correction for salt effect (p. 349).

in an unsatisfactory state, there is little doubt that the general conclusions are not far from the truth, and it is therefore of interest to compare them with certain other workers' views.

Raschig's ideas on the general course of the oxidation of hydroxylamine are put forward in detail in his "Stickstoff- und Schwefel-Studien," 1924. They are, briefly, that the first stage consists in the slow formation of the radical NH·OH, which unites with a similar radical to give  $\begin{array}{c}\mathrm{H{\cdot}N{\cdot}OH}\\ |\\ \mathrm{H{\cdot}N{\cdot}OH}\end{array}$. After this point a variety of possibilities is supposed to arise and the persistence of any one type of molecule will depend not only on its inherent stability but also on the rapidity with which it may be further oxidised. Thus, in the next phase one might have  $\begin{array}{c}\mathrm{N{\cdot}OH}\\ \|\\ \mathrm{N{\cdot}OH}\end{array}$ or  $\begin{array}{c}\mathrm{H{\cdot}N}\\ |\\ \mathrm{H{\cdot}N}\end{array}\!\!>\!\mathrm{O}$ according as the dihydroxyhydrazine could be further oxidised before it dehydrated or not, and in the latter case further oxidation would give hyponitrous acid,  $\begin{array}{c}\mathrm{H{\cdot}N}\\ |\\ \mathrm{HO{\cdot}N}\end{array}\!\!>\!\mathrm{O}$, which would decompose to nitrous oxide if nothing were present to oxidise it more rapidly than it could decompose. These views appear to the author to have the great advantage that they explain the variety and varying proportions of the end-products.

The results described herein, however, indicate that the first *measurable* stage involves, in effect, the removal of two hydrogen atoms from each molecule of hydroxylamine, because undoubtedly two molecules of ferric salt are implicated, and it is difficult to see what (if any) preliminary rapid reaction, save the formation of a "critical complex," could lead to a subsequent measurable termolecular reaction. The molecule thus appears to be oxidised to the stage represented by the hypothetical nitroxyl or nitrous oxide, although the latter is only produced as the result of secondary changes. These views agree, to a certain extent, with the earlier opinion expressed by Raschig, when dealing with the estimation of hydroxylamine by ferric salts, that an intermediate compound (possibly nitroxyl) of moderate stability is produced, which delays the completion of the reaction for analytical purposes (*Z. angew. Chem.*, 1904, **17**, 1411).

As will be seen from the experimental portion of this paper, there is no foundation for Brönsted's statement, quoted on p. 337, that the reaction under discussion is not appreciably susceptible to salt effect, although the magnitude is not so great as he appeared to look for. Actually there is a definite negative salt effect, which would, according to Brönsted, indicate reaction between ions of opposite polarity; but it is doubtful whether his hypotheses, which are based on comparatively simple cases, can be extended to such complicated reactions as the present.

The hydroxylamine was always employed as hydrochloride, which had been recrystallised and freed from excess acid; both this salt and the ferric chloride would give a trace of free hydrochloric acid by hydrolysis, so that, in experiments with no added acid, there would always be a trace of free acid initially, which would slightly affect the earliest velocity coefficients.

EXPERIMENTAL.

All the experiments were carried out at 25°, with the exception of those necessary to find the temperature coefficient. Time is expressed in minutes throughout. The details call for no special description except in regard to the analytical method. The course of the reaction was followed by the estimation of unchanged ferric iron. The process was based on two facts: (1) hydroxylamine has no effect on iodine during the short time necessary for titrations provided that considerable mineral acid is present—sulphuric acid sufficient to be in normal concentration throughout the titration was found to fulfil this condition; and (2) ferric iron can be estimated consistently and fairly accurately by titration of iodine liberated from potassium iodide, if a trace of cuprous iodide is present as recommended by Hahn and Windisch (*Ber.*, 1923, **56**, 598). The equilibrium which tends to be set up ($Fe^{\cdots} + I' \rightleftharpoons Fe^{\cdot\cdot} + I$) is displaced by titration of iodine as fast as it is formed, and the presence of the cuprous salt accelerates the reaction (presumably by more rapid reduction of ferric salt and continuous re-formation of cuprous salt) to such an extent that titrations can be completed in the ordinary time instead of lasting for several minutes, as in the absence of cuprous salt. Although the method has been criticised (Rupp, *Apothek. Z.*, 1924, **39**, 422), the author's experience is that it is useful and gives results about 1 part in 300 parts high (with titres of 40 c.c.), but this error might be reduced if precautions were taken against the aerial oxidation of the solution containing hydriodic acid and ferrous salts.

The starch–iodine coloration returns after a few minutes in the titrations made during actual runs, and rather less rapidly in controls with ferric salts in the absence of reaction products. The difference is attributed to the presence of traces of nitrous acid.

As the result of many duplicate runs, it may be stated that experiments are reproducible almost invariably within about 0·1 c.c. on titres of usually 30 or 40 c.c.

The behaviour of a complex of the type suggested on p. 342 in such titrations is, of course, uncertain; it might react either as ferrous or as ferric iron. The latter possibility is improbable, for the apparent rate of initial change would then be far less than the actual, and would subsequently tend to increase temporarily as the complex broke down; the apparent course of the reaction shows such enormous diminution in velocity that it is more likely that the complex reacts as a ferrous compound.

A control was made to ascertain whether hydroxylamine in nearly neutral solution exercised any oxidising effect on ferrous iron, such as it exerts in alkaline solution. The result was definitely negative.

The curves obtained by plotting experimental differential velocities against x change so rapidly that they are not capable of "smoothing." The velocities shown in the tables were therefore obtained by plotting x against the square-root or fourth-root of time, according to circumstances. The fairly flat curve thus obtained was smoothed and the values of $\sqrt{t}$ or $\sqrt[4]{t}$ corresponding to a series of values of x were read off, and, from the values thus obtained, a further curve was constructed, on the basis of $v = \delta x/\delta t$, showing the relation between x or $(a - x)$ and v. Even this method leaves considerable uncertainty in the early stages of experiments of type I. The integrated velocity coefficients are based on unsmoothed values.

Salt Effect.—Experiments similar to No. 4 were made with the addition of $M/10$- and $M/5$-ammonium sulphate; they gave results uniformly slower in the proportion 1·14 and 1·30, respectively. A similar experiment comparable with No. 2 gave a slightly greater depression. The primary object of this type of experiment was to find what correction, if any, should be applied to experiments of types III and IV (in which the ferrous salt had been added, for convenience, as ferrous ammonium sulphate), in order that they should be comparable with one another and with those of other types. When a definite effect was found, it was essential to make a few other determinations in order to obtain an estimate of that due to ferrous sulphate. An experiment parallel with No. 12, but having $M/10$-ammonium sulphate present, in addition to the $M/10$ already added as the double salt, showed a reduction of velocity in the ratio 1·17 to 1, whereas from the foregoing one would have expected a ratio of 1·30 to 1·14, *i.e.*, 1·14 to 1—a result which is as near as can be expected from the graphical methods which have to be used in the absence of really satisfactory velocity coefficients, and which shows that the salt effect is fairly consistent.

$M/15$-Aluminium sulphate gave a depression identical with that of $M/5$-ammonium sulphate and, therefore, twice as great as the $M/10$-ammonium sulphate to which it is equivalent; this result is characteristic of the ion of higher valency.

TABLE I.

< = values rising during expt. > = values falling during expt. (c) = approx. constant at value annotated.

	Expt.	*a*.	$\frac{1}{2}b$.	*h*.	*f*.	$k_1 \times 10^5$. Integrated.	$k_1 \times 10^5$. Differential.	$k_2 \times 10^6$. Integrated.	$k_2 \times 10^6$. Differential.	% completed.
Type I.	1	0·200	0·0500	—	—	500>250	470>220	150<245	190<260	80
	2	,,	0·1000	—	—	500>200	350>200 (*c*)	160<240	230 (*c*)	50
	3	0·100	0·0500	—	—	800>360	500>370 (*c*)	140<265	210<260	60
Type II.	4	0·200	0·0500	0·1000	—	164>120	140 (*c*)	180<220	190<250	70
	5	,,	,,	0·2000	—	89 (*c*)	88 (*c*)	180<225	185<220	60
	6	0·100	,,	0·2000	—	89 (*c*)	89 (*c*)	180 (*c*)	180<210	35
	7	0·200	,,	0·8000	—	24 (*c*)	—	192 (*c*)	—	25
	8	0·100	0·0250	0·2000	—	84 (*c*)	84 (*c*)	170 (*c*)	170<200	50
	9	,,	0·0500	0·8000	—	22 (*c*)	—	176 (*c*)	—	10
	10	0·200	0·1000	0·8000	—	24 (*c*)	—	192 (*c*)	—	15
	11	0·040	0·0100	0·8000	—	21 (*c*)	—	168 (*c*)	—	10
	22	0·200	0·0500	0·0500	—	210>170	190>155	160<240	180<240	75
Type III.	15	0·200	0·0500	—	0·1000	85<260 (*c*)	65<270>240	0(?)<200	0<250	70
	23	,,	,,	—	0·0500	220<290>250	320>215	0(?)<215	115<230 (*c*)	75
Type IV.	12	0·200	,,	0·1000	0·1000	169 (*c*)	169 (*c*)	200<230	200<255	20
	13	,,	,,	0·1000	0·2000	140 (*c*)	145 (*c*)	150<182	170<230	30
	14	,,	,,	0·2000	0·1000	97 (*c*)	97 (*c*)	195<220	210<250	30
	17	,,	,,	0·0500	0·1000	195>170	200>140	110<190	110<195	60
	18	,,	,,	0·1000	0·0500	148 (*c*)	150>130	171<215 (*c*)	165<240	55
	19	,,	,,	0·0500	0·0500	240>180	240>155	145<210	150<215 (*c*)	60
	20	0·125	0·0625	0·1125	0·0750	140 (*c*)	138 (*c*)	170<190	160<215	25
	24	,,	,,	0·0750	0·0750	205 (*c*)	220>185	170<220	195<260	35
	25	,,	,,	0·0750	0·0375	222>200	220>190	192<260	190<290	55
	26	,,		0·0375	0·0375	330>260	310>220	195<245	180<255	55
	31	,,	,,	0·1125	0·0375	155 (*c*)	155 (*c*)	200<250	200<265	35
	32	,,	,,	0·0375	0·0750	250 (*c*)	255>220	120<200	145<230	35

Zinc ammonium sulphate was chosen as being best suited for comparison with the ferrous ammonium sulphate. For $M/5$- and M/10-solutions it showed depressions in the proportions 1·54 and 1·31 respectively. As these are consistent with the foregoing results, the general trend was adopted as the basis for corrections of all experiments of types III and IV, and the factors by which velocities are multiplied (or times divided) are :

for 0·2000 molar ferrous ammonium sulphate	1·54
0·1000 ,, ,, ,, ,,	1·30
0·0750 ,, ,, ,, ,,	1·22
0·0500 ,, ,, ,, ,,	1·14
0·0375 ,, ,, ,, ,,	1·11

A comparison of, for example, Expts. 10 and 11 does not indicate the relatively large salt effect which might be expected from a five-fold change in the concentration of the tervalent ferric salt, and, for this reason, no attempt has been made to correct for such salt effect.

Experiment I. $a = 0{\cdot}2000$, $\frac{1}{2}b = 0{\cdot}0500$.

			Integrated.		Differential.	
t.	x.	$v \times 10^5$.	$k_1 \times 10^5$.	$k_2 \times 10^6$.	$k_1 \times 10^5$.	$k_2 \times 10^6$.
*0·33	0·0212	—	510	122	—	—
*0·83	0·0274	900	489	151	468	193
*1·50	0·0316	500	450	162	385	180
*2·17	0·0348	370	437	180	378	198
*3·67	0·0390	260	402	185	375	219
5	0·0432	190	—	—	382	247
*9·7	0·0480	125	346	198	360	259
12	0·0516	80	—	—	300	232
*20	0·0556	55	313	210	275	230
21	0·0570	50	—	—	277	237
30·5	0·0604	37	284	206	262	237
45	0·0650	25	289	230	250	240
70	0·0700	16	273	236	232	244
140	0·0780	8	252	247	223	260
160	0·0794	—	246	245	—	—

Experiment 5. $a = 0{\cdot}2000$, $\frac{1}{2}b = 0{\cdot}0500$, $h = 0{\cdot}2000$.

*0·52	0·0042	—	91	182	—	—
*1·7	0·0074	193	92	191	88	186
*4·3	0·0114	107	94	198	84	182
6	0·0126	94	—	—	85	184
*8·6	0·0146	77·5	(82)	(176)	86	191
13	0·0178	60	—	—	88	202
*21	0·0220	42·5	88	197	87	203
23	0·0228	40	—	—	88	205
*38	0·0280	27	90	206	86	210
54	0·0316	22	—	—	89	220
*59	0·0326	20·5	87	204	88	220
91	0·0380	14·5	—	208	87	225
170	0·0470	8	89	224	82	220
284	0·0544	—	85	234	—	—
410	0·0596	—	84	224	—	—

* Indicates that these values are taken from an experiment at 15·5° and the time is corrected for the temperature coefficient.

Experiment 18. $a = 0{\cdot}2000$, $\frac{1}{2}b = 0{\cdot}0500$, $h = 0{\cdot}1000$, $f = 0{\cdot}0500$.

(All values of v, k_1, and k_2 should be multiplied by 1·14, the salt effect factor.)

5	0·0048	82·5	142	162	134	143
12	0·0098	63·0	134	145	133	152
23	0·0158	47·0	134	152	134	165
39	0·0222	32·8	134	161	128	171
76	0·0316	20·3	129	163	126	185
110	0·0374	14·7	128	174	122	190
171	0·0448	10·0	125	182	119	199
255	0·0518	6·8	123	189	116	207
320	0·0557	5·4	122	190	114	209

(The product hf increases four-fold, and h^2f seven-fold during the run.)

Summary.

1. The rate of reaction *after the early stages* is directly proportional to the concentration of hydroxylamine and to the square of that of ferric chloride, and inversely proportional to the concentration of ferrous salt and to the square of the hydrogen-ion concentration.

2. The most probable interpretation is that reaction proceeds by way of an intermediate equilibrium involving a complex of the type shown: $2Fe^{\cdot\cdot\cdot} + NH_3OH^{\cdot} \rightleftharpoons Fe^{\cdot\cdot} + 2H^{\cdot} + (NOH,Fe,H)^{\cdot\cdot\cdot} \longrightarrow N_2O$, etc.

3. The abnormal temperature coefficient of 6·5 for a 10° rise would thus be partly due to a more favourable displacement of the equilibrium.

4. "Salt effect" is negative—reaction velocity is depressed by the addition of indifferent salts.

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