

LXIV.—*The Specific Action of a Mixture of Sulphuric and Nitric Acids upon Zinc in the Production of Hydroxyamine.**

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ZINC dissolves in dilute nitric acid, forming nitric oxide, nitrous oxide, ammonium and zinc nitrates, a little nitrogen, and sometimes a trace of hydroxyammonium nitrate. Should it dissolve so far as to neutralise or nearly neutralise the acid, zinc nitrite is also formed. By mixing much sulphuric acid with the nitric acid, the dissolution of the zinc produces sulphates in place of nitrates and nitrites, hydroxyammonium and ammonium sulphates, nitrous oxide and a little nitrogen, little if any nitric oxide, and, lastly, hydrogen. When nitric acid, in moderately small quantity relative to the sulphuric acid present, is added to dilute sulphuric acid freely effervescing on zinc, not only are the above nitrogen products formed, but the intensity of the effervescence becomes so greatly reduced as to suggest an inhibitory action by the nitric acid, until consideration is given to the facts that the temperature rises, and the zinc is corroded even faster than before.

To learn more than these already known facts, showing that a mixture of the acids exerts an action which is not the mere sum of the actions of the acids apart, and to endeavour to determine the cause of this difference in action, we have made a great number of experiments. Many of these will not be described now, because the results

[* NOTE.—In this and succeeding papers, the authors use "hydroxyamine" in place of the well-known word hydroxylamine, without any statement as to why they consider a change in the established nomenclature to be desirable.—THE EDITOR.]

obtained have led to other experiments which supersede them. Nor shall we treat our subject in the order in which we followed it experimentally, but place our observations in what now appears to us the best order to support such conclusions as we have come to. We had hoped to present to the notice of the Society such a valuable memoir on our subject as industry and care seemed likely to enable us to prepare, but in this we have been disappointed, such an undertaking having proved too great for our present resources. We now offer this paper as only a small contribution to the knowledge of the reactions between zinc and the two acids. Of the difficulties we have met with, we shall say more in a later part of the paper.

Rate of Action of Sulphuric Acid upon Zinc.

Experiments made to ascertain the weights of zinc dissolved by the separate acids, as compared with those dissolved by a mixture of the acids, have given important results. Those yielded by zinc and sulphuric acid only have an interest independent of the purpose for which they were instituted.

“Every one knows that, in making hydrogen, more gas is obtained, within certain limits, if the acid be stronger, the temperature higher, the quantity of zinc greater, and the time during which the action continues longer; but what relation the quantity of gas bears to each of these conditions is at present wholly unknown.” (A. Vernon Harcourt.) This statement, made nearly 20 years ago, may, so far as we know, be as truly made to-day as when it was uttered. Writing on such a familiar subject as this, we may add, in continuation, that “every one knows” how capricious the reaction of zinc and dilute sulphuric acid appears to be, sometimes setting in almost fiercely, and at others manifesting itself so deliberately as to try the patience of the operator needing the hydrogen. And scarcely less well known is the dictum that the zinc is the more resisting the purer it is, so that with absolute purity we should expect complete passivity. But that the variation in the activity of zinc would be so great as it has proved in our hands, and so sensitive to inappreciable variations in the circumstances under which this activity is developed, will hardly have been inferred by any one.

A large piece of sheet zinc was procured, which had formed part of the lining of a packing-case. It was merely tarnished and spotted by rain on one side, and uniformly, but slightly, weathered on the other. Rejecting a large margin of it all round, the sheet was cut into rectangles 128×86 mm., approximately. For about 45 hours, these pieces were kept wholly immersed in weak alcoholic potash, to cleanse them from grease and oxide. They were then rinsed, pressed between

folds of blotting paper, and gently heated for a minute, in order to dry them thoroughly and quickly. They then presented a uniform and satisfactory appearance, with one side duller than the other, as at first. A small hole was pierced in each, near one margin, that it might afterwards be suspended by a string. Those to be used were weighed, and then fitted with a loop of string. Throughout the preparation of the sheets after they had been immersed in the potash, care was taken not to touch them with bare fingers, except lightly at the edges. The approximate area of the surfaces of a sheet was 2.2 square decimeters, and mean weight 21.527 grams, with the range of a third of a gram, excepting one sheet which weighed only 20.96.*

The dilute sulphuric acid needed was made in large quantities at a time. The degree of dilution was such that 100 c.c. contained about 15 grams of hydrogen sulphate. Each sheet was wholly immersed in a separate and similar vessel, containing 2400 c.c. of the acid. The quantity of acid was thus so large, relative to the amount of metal dissolving during the experiment, that the diminution of its strength during the progress of the experiment had, and could have, no practical effect in modifying the results. Indeed, in some cases, where a solution was used over again, as a convenience, the strength was still essentially unchanged, for the fresh solution was calculated to be sufficient to dissolve 234 grams of zinc, and had only dissolved when taken for second use a quantity less than 1 gram. Time observations were made with care, and a very few seconds must have been the limit of error. In some cases, the limit was certainly much narrower, because experiments were made simultaneously in this way:—When two sheets were to be immersed, they were held by their loops over their vessels, one in each hand, and then both immersed and the time taken all at once, and by one operator. In a similar way, they were taken out, and plunged into water or fresh acid, according to the plan of the experiment. Or else, two sheets were immersed and removed together, by hanging two on the ends of a glass rod held horizontally in one hand over two vessels of acid; in this way three or four sheets could be tried at once, by using both hands. In rinsing the sheets, the string-loop was quickly removed by scissors. After rinsing, the sheets were pressed again between folds of blotting-paper and dried, as at first, before weighing. Although in most cases a black residue coated the sheets, easily rubbed off, it did not visibly come off on to the blotting paper, and, even had it done so slightly, the accuracy of the experiment would not have been affected, since we only weighed to centigrams. The experiments were made in cold weather. The rise in temperature of

* Sheet-zinc is far from being of uniform thickness throughout the piece.

the mixture during reaction was but slight, in consequence of the large volume of the solution.

One of the sheets of zinc was immersed for five minutes in 2400 c.c. of acid and then weighed. It was again immersed for five minutes in another 2400 c.c. of acid and weighed; and again in a third and in a fourth quantity of acid. The losses in weight were successively—

1.04, 2.08, 3.21, and 5.00 grams,

making a total of $11\frac{1}{3}$ grams in twenty minutes.

A second sheet was treated in the same way, except that a fifth immersion of five minutes was made, and caused it to be eaten away at the edges and into small holes, and therefore to be diminished in extent of surface. The losses were—

0.43, 1.26, 2.39, 4.25, and 7.00 grams,

or in twenty minutes $8\frac{1}{3}$ grams, and in twenty-five $15\frac{1}{3}$.

Four sheets were immersed at once in four vessels of acid, and in five minutes transferred, one to water, the rest to fresh acid, 2400 c.c. in each vessel as before. Again in five minutes the three sheets were removed, one to water, the other two to two of the vessels of the acid already used once in the first five minutes, and still as good as fresh acid. In five minutes more these two were removed, the one into water, the other into one of the vessels of acid already used once in the first five minutes. The losses for sheets A, B, C, and D are given in the table. Four sheets, A', B', C', and D', were similarly treated.

Time.	Sheet.	Loss.	Sheet.	Loss.
5 minutes....	A.	0.55 gram	A'....	0.23 gram.
10 „ 	B.	2.08 grams	B'....	1.74 „
15 „ 	C.	6.27 „	C'....	2.99 grams.
20 „ 	D.	9.65 „	D'....	11.03 „

These experiments with four sheets are free from the objection that might be raised against those conducted on a single sheet, namely, that the surface of the zinc may have been materially affected in some way by the exposure to air during the intermediate drying and weighing, and they thus serve to show that the single sheet was not appreciably affected in the way suggested.

The results of the preceding experiments may be tabulated, so as to make more prominent the wide variation in the quantities dissolved in equal times of equal-sized pieces of the same large sheet of zinc.

5 min.	10 min.	15 min.	20 min.
0·23	1·69	2·99	8·33
0·43	1·74	4·08	9·65
0·55	2·08	6·27	11·03
1·04	3·12	6·33	11·33

The quantity of zinc dissolved in a given time is here seen to have been in one case $1\frac{1}{3}$, or $2\frac{1}{3}$, or 2, or $4\frac{1}{2}$ times what it was in another; taking the extreme results with the ten sheets, whilst in other cases the quantity dissolved in one closely approached that dissolved in another.

It will also be seen how greatly the rate of dissolution increases with the duration of the immersion, and how variable this rate of increase may be in different cases. Thus, while in one case 5 grams were dissolved in the fourth five minutes against 2 grams off the same piece in the second five minutes, in another case $4\frac{1}{4}$ grams were dissolved in the fourth five minutes against $1\frac{1}{4}$ grams in the second five minutes. If a comparison is made of the zinc dissolved in the first five minutes, this difference will be seen to be even much greater.

An acid more dilute than the very strong 15 per cent. acid gave results showing more remarkable disproportion in the quantities of zinc dissolved in equal times under apparently the same conditions. Two sheets cut from a piece of zinc, not the same as that of the previous experiments, lost by 15 minutes' immersion in acid, the one in 15 per cent. acid 6·72 grams, the other in $7\frac{1}{2}$ per cent. acid only 0·57 gram. The experiment repeated with fresh vessels of acid and fresh sheets of the same zinc gave almost identical results—6·72 and 0·56 grams, thus not only confirming those first obtained with this zinc, but contrasting in their uniformity with the varied results obtained with the other zinc, and for no evident reason.

We knew that all zinc could not thus be inactive to acid—that is, could not have more than 20 decimetres of surface exposed for a quarter of an hour to a $7\frac{1}{2}$ per cent. solution of sulphuric acid measuring nearly $2\frac{1}{2}$ litres, and yet only lose half a gram in weight! We therefore repeated the experiment, using other zinc. This time the result was no less surprising, but in a different way. In 15 per cent. acid one sheet lost 4·30 grams, and in $7\frac{1}{2}$ per cent. acid the other lost 2·43 grams, that is actually a little more than half as much as the one in the acid of double strength. A fresh sheet of the zinc that had lost in 15 minutes only 0·56 gram in 7 per cent. acid against 6·72 grams in 15 per cent. acid, was immersed for 20 minutes in 3 per cent. acid, and found to lose only 0·09 gram. A sheet cut from still another piece of zinc lost, when immersed for 15 minutes in 3 per cent. acid, ten times as much, namely, 0·90 gram.

The experiments described were not executed in the order in which we have here given them. Those first given, in which on two occasions a single sheet was immersed repeatedly, and again on two occasions, in which four sheets were immersed at the same moment, were our last ones. The others preceded them, and had led us to the conclusion that the differences in activity we had observed were due to our having used different makes of zinc, so that when we instituted our later experiments with sheets all cut from one piece of zinc and prepared alike and together, we fully expected to get uniform behaviour from these sheets. How far we were from doing so has been pointed out, and, seeing how pieces of the same zinc may differ widely in chemical activity, we must now add that what we had to treat as different makes of zinc because we had found them behave differently and had received them in separate pieces, may after all have been actually or essentially all of one make. Before we had recognised this, we had analysed the active and inactive zinc, and found no key to their difference in the degree and nature of their impurities. The selected specimen of active zinc contained 1.09 per cent. lead, the inactive zinc 1.22 per cent. lead. They both contained a very little iron, something less than 0.1 per cent. The active zinc gave indications of the presence of a trace of arsenic, the inactive hardly gave such indications. We shall have more to say later on respecting the influence and want of influence of the impurities of zinc on its activity.

Granulated zinc also sometimes shows remarkable differences in activity towards sulphuric acid, and this is of special importance in our present inquiry, because we have employed the zinc in this form in nearly all experiments on the reduction of nitric acid by zinc. We have, however, not attempted any quantitative determinations of these differences. All the granulated zinc we have employed in our experiments, and the quantity has been large, has been granulated by ourselves, and we soon found the necessity there was to keep the several batches apart, in order to get uniform results in comparative experiments. We shall return to this question in another section of this paper, and will only mention here that while a granule from one batch would at once set up effervescence when thrown into dilute sulphuric acid, one from another batch would remain passive perhaps for several minutes, and then only very gradually become active.

We do not believe that we have anything new to add in explanation of the great variability in activity of zinc towards sulphuric acid. The current view is probably correct, that pure zinc would prove to be passive in dilute sulphuric acid, and that ordinary zinc becomes active by the formation of innumerable minute galvanic couples on its surface. The temporary passivity, and the irregular rate at which

this is overcome by the acid, as well as the continuously increasing rate at which the acceleration in activity occurs, may be attributed to differences and changes in the degrees of contact of the zinc with the particles of the lead or other foreign metal. By rolling and cutting, or by surface tension brought into action during granulation, the metal becomes compressed on the surface, and intimate contact is made between the heterogeneous particles forming it. Electric polarity can therefore be but slightly preserved between these particles, and so the zinc shows itself nearly inactive for a time. Dissolution of the zinc, however, partly insulates the particles of lead, which then can form couples of marked power with the zinc, and increase the rate of its dissolution. Thus, as dissolution proceeds, more couples are brought into activity, and those already active rendered more so, with the result of causing an ever-increasing rate in the dissolution of the zinc.

With zinc so variable in activity towards sulphuric acid, it does not seem possible to determine with any certainty the relations of the amount of action between the metal and the acid to the extent of their contact, to the dilution of the acid, to the volume of the solution, temperature, time, and other circumstances. There are, moreover, other obstacles to the attainment of trustworthy measurements of the influence of these circumstances. The uniform movement of the liquid over the metal surface, which would be necessary for such purposes, is unavoidably interfered with by the varying extent of effervescence, and by variations in temperature caused by the reaction itself. Uniformity of temperature is also impossible, for although external application of heat or cold may effect something, it can hardly influence the great changes in temperature which must occur at the very surface of contact of the metal and acid, where, of course, the chemical action takes place, and is subject to modification. It seems unnecessary to extend this statement of obstacles.

Rate of Action of Nitric Acid upon Zinc.

Experiments were made with nitric acid similar to those with sulphuric acid, already described. Zinc, size of sheets, preparation of the zinc, volume of the dilute acid, vessels, &c., were the same, but in place of the 15 per cent. solution of sulphuric acid, a solution of 5 grams of hydrogen nitrate in 100 c.c. was used. The results were not remarkable for their differences, as were those with the use of sulphuric acid.

A single sheet was immersed four times for five minutes successively, each time in a different vessel of the nitric acid (2400 c.c.), and

washed, dried, and weighed between each immersion. Another sheet was similarly treated. The losses sustained were—

I.....	2.99	3.69	4.02	3.12
II.....	3.16	3.46	4.02	3.59

making totals, I, 13.82; II, 14.23 grams; or in 15 minutes from the beginning, I, 10.70; II, 10.64. The zinc does therefore vary in activity according as it has been a longer or shorter time in the nitric acid, but much less so than when the acid is sulphuric acid. In the fourth five minutes, the activity proved to be distinctly *less* than it had been, a result due apparently to the mechanical protection given to the unattacked metal by a coat of residual lead, as well as to diminished size of the sheet through its having corroded into holes and at the edges.

The vessels of acid already used* in the first of the two experiments were ranged in a row, and four sheets of zinc immersed, one in each, for five minutes, and the losses weighed.

III, 2.84; IV, 2.55; V, 2.42, and VI, 2.61 grams,

were respectively lost, showing what small deviations from uniformity are found as compared with those when sulphuric acid acts upon zinc. During the reaction there was in every case moderate effervescence and a faint smell of nitrous vapours, but no distinct red fume.

Using a 1 per cent. nitric acid, the loss by the zinc was more variable, but our experiments were not of such accuracy as to justify us in giving their details. The quantity dissolved was often about a fifth of that dissolved in the first five minutes by the 5 per cent. nitric acid, but sometimes less.

Rate of Action of the Mixed Acids upon Zinc.

The rate of action of the mixed acids upon zinc is very different from the sum of the rates of action of the separate acids. This important fact is shown by the experiments which follow.

Two sheets of zinc were first immersed for five minutes, each in its own vessel, in 2400 c.c. of 15 per cent. sulphuric acid, in order to measure, and at the same time to raise, its activity. Sheet I thus lost

* The acid, already once used, was perhaps a twentieth less strong than at first, and certainly slightly weaker in one than in another vessel, but the results show the unimportance of these differences, so great was the excess of acid over that required. It was used instead of fresh acid, merely for convenience and economy, the purest commercial acid having been taken, and that is rather costly here in Japan.

0.43 gram, and sheet II 0.50 gram. They were then immersed for a second five minutes, this time in the mixture of three measures of 15 per cent. sulphuric acid and one measure of 5 per cent. nitric acid, 2400 c.c. to each sheet in a separate vessel.

Of sheet I, 10.11 grams dissolved, and of sheet II, 8.67 grams dissolved in the five minutes. With such a rate of dissolution, we saw that the power of the acid solution might have become markedly less in the course of five minutes through the destruction of much of the nitric acid, and the neutralisation by zinc, ammonia, and hydroxyamine of say 20 grams of sulphuric acid. Influencing the rate of dissolution of the zinc in an opposite way, there was to be considered the effect of the perhaps material, though unnoticed, rise of temperature which might have occurred. We therefore made two other experiments, differing from the preceding only in 8000 c.c. of the mixed solutions being taken instead of 2400 c.c. in each case. The rise in temperature was here, as in earlier experiments, not greater than 2° , and the slight weakening of the solution in the five minutes became now insignificant for our purpose. By the preliminary treatment with 15 per cent. sulphuric acid, sheet III lost 0.51 gram, and sheet IV 0.23 gram. In the mixture, III lost 10.88 grams immersed five minutes in 8000 c.c., and IV lost 11.56 grams by a similar immersion in another 8000 c.c. Further immersion of these sheets in the mixed acids caused their entire dissolution in three or four minutes.

The mixture of acids which thus in five minutes dissolves about 11 grams of zinc from a surface of 2.2 cub. decim. *is of a strength to dissolve not a fifth of this amount if each acid acts independently of the other.* For, as a solution of sulphuric acid, it is only three-fourths of the strength of that which by itself dissolves in the second five minutes about 1.5 gram, whilst as a nitric acid solution it has only one-fourth of that which by itself dissolves in the second five minutes about 3 grams. The combined effect should therefore by calculation be $\frac{3}{4} \times 1\frac{1}{2} + \frac{1}{4} \times 3 = 1\frac{1}{8}$, say 2 grams of zinc dissolved.

Before proceeding to discuss the nature of the great difference between the acids when apart and when mixed, in their power to dissolve zinc, we shall detail some experiments on the duration of effervescence, which agree as to their results with those we have just described.

On the Shortening of the Duration of the Effervescence between Zinc and Sulphuric Acid by adding Nitric Acid.—Not only does the addition of nitric acid to sulphuric acid lessen the degree of the effervescence with zinc, but it materially shortens its duration. This is rendered certain by the experiments on the rate of dissolution of zinc in the mixed acids, but its exhibition by direct experiment is not unimportant.

In each of eight experiments, we poured 250 c.c. of a solution of sulphuric and nitric acids upon 45 grams of granulated zinc, and noted—the time at which we did so, the time when effervescence practically ceased, and the temperature of the mixture, at starting, at six minutes, at ten minutes, and at fifteen minutes. In every experiment, the quantity of sulphuric acid was 10·7 grams. The quantity of nitric acid was very much less, and varied, being 1·375 gram in (I), seven-tenths of this in (II), five-tenths in (III), three-tenths in (IV), one-tenth in (V) and in (VA), and none at all in (VI) and in (VIA). The largest quantity of nitric acid used was to that of the sulphuric acid as one equivalent to ten. In six of the experiments the solution was poured on cold, but in the two marked (A) it was poured on warm, and the temperature of the mixture artificially maintained equal to that of experiment (I) as near as might be. We give the results in tabular form:—

No.	Nitr. acid.	Efferv. over.	Temperatures.			
			0 m.	6 m.	10 m.	15 m.
I....	1·0	12 m.	10°	40°	41°	—
II....	0·7	20 „	„	38	40	—
II....	0·5	26 „	„	35	37	—
IV....	0·3	34 „	„	30	32	35°
V....	0·1	44 „	„	26	30	32
VI....	0·0	53 „	„	23	27	29
VA....	0·1	32 „	„	made 40° to 42° throughout.		
VIA....	0·0	35 „	„	made 40° to 42° throughout.		

The effect of the nitric acid in raising the temperature is very marked, and the repetition of (V) and (VI), as (VA) and (VIA), shows the very considerable effect of increased temperature in shortening the duration of effervescence. But when the (A) experiments are compared with the first two or three experiments, with which they agreed in temperature, the effect of the nitric acid in shortening the time of effervescence is seen to be still very marked, independently of any change in temperature.

It thus appears that, even after allowance is made for the effect of greater rise in temperature during the action of the acids upon the zinc, the presence of nitric acid greatly hastens the neutralisation of sulphuric acid by zinc.

The Nascent Hydrogen and other Hypotheses in Explanation of the Action of a Mixture of Sulphuric and Nitric Acids upon Zinc.

All the ways that can be suggested as those in which the acids

may prove to be more active towards zinc when mixed than when separate, appear to be included in the following :—

- I. Nitric acid promotes contact of the sulphuric acid with the zinc by consuming its liberated hydrogen while yet nascent.
- II. Sulphuric acid hastens the reduction of the nitric acid by the zinc, by decomposing nitrates, and thus keeping it free.
- III. Sulphuric acid so acts upon the zinc as to make it more active towards the nitric acid.
- IV. Nitric acid so acts upon the zinc as to make it more active towards the sulphuric acid.
- V. Sulphuric acid intensifies the action between the zinc and the nitric acid, by acting upon the nitric acid and combining with it.
- VI. Nitric acid intensifies the action between the zinc and the sulphuric acid, by acting directly upon the sulphuric acid.

We proceed to consider whether, and to what extent, the dissolution of the zinc is quickened in each of these ways, taking them in the above order.

I. *As to Nitric Acid Promoting Contact of the Sulphuric Acid with the Zinc by Consuming its Liberated Hydrogen while yet Nascent.*—The phenomena observed on adding a little nitric acid to sulphuric acid effervescing on zinc, naturally suggests that hydrogen continues to be developed, but is now seized by the nitric acid before it has time to become gaseous. But the difficulties in the way of accepting the nascent hydrogen hypothesis have already been stated in part (this Journal, 43, 443). In some cases it offers an explanation of the formation of bodies which in other cases are certainly formed without the aid of nascent hydrogen. Ammonia is abundantly produced from nitric acid by the zinc-tin metals in absence of sulphuric or other acid. Hydroxyamine is formed from nitric oxide by a mixture of stannous chloride and hydrochloric acid (v. Dumreicher), and such a mixture never liberates hydrogen. If the action of sulphuric acid upon zinc in the presence of nitric acid subserved the reduction of the latter to the extent required, by supplying nascent hydrogen, no hydrogen gas should escape from a mixture of not more than 7 mols. of sulphuric acid to 2 mols. of nitric acid, when acting upon zinc; yet, as a fact, it escapes freely when the proportion of sulphuric acid is much smaller. This objection to the nascent hydrogen hypothesis, which was insisted upon in the paper already referred to, seems to be of the weightiest character, for at the moment the hydrogen of the sulphuric acid is nascent, it is perfectly mixed with the nitric acid, which it fails to reduce.

There is, however, an explanation, which it is possible to offer, of

this hypothesis. This is, that nascent hydrogen may resemble ozone when exerting its activity, and combine in part only with other bodies and in part become ordinary inactive gas. But then, the invariable univalency of the hydrogen-atom seems of itself sufficient to negative this supposition. Besides, were nitric acid thus able to take merely a certain fraction, such as a third, of the nascent hydrogen, leaving the rest to become gaseous, it should be possible to greatly increase, if not double, the rate of the reduction of the nitric acid, by doubling the quantity of sulphuric acid mixed with it. That this is by no means the case will be shown in a later section.

In contact with zinc, nitric acid, when alone, is rapidly converted into ammonia and other reduction-products. For the nascent hydrogen hypothesis to be true, it seems necessary to assume that in presence of sulphuric acid, nitric acid ceases to be reduced by zinc directly, and suffers reduction instead by the nascent hydrogen of the sulphuric acid. But, as we have already described, the sulphuric acid in contact with zinc is much more rapidly neutralised in presence of nitric acid than in its absence, and the zinc is much more rapidly dissolved. The hypothesis affords no explanation of this rapid action, and the nitric acid evidently does not wait for hydrogen to be liberated by the simple action of the sulphuric acid upon the metal, but either acts freely itself upon the zinc and thereby suffers reduction, or makes, in some way, the action between the zinc and sulphuric acid much more intense, and thus a more prolific source of hydrogen than it is ordinarily.

One way out of the difficulty suggests itself, but this will not stand careful consideration. The hydrogen being consumed in the nascent state by the nitric acid instead of becoming gaseous on the surface of the zinc, the zinc will remain in contact with the solution instead of being kept apart by a layer of gas, and will therefore be dissolved more rapidly. But it will quickly be seen that the thinnest layer of gas would be as effective in breaking contact between the metal and the liquid as the thickest, and in all cases there must be a superabundance of gases developed to operate in this way, if they ever do so. Further, a layer of liquid in contact with the metal must almost at once become inactive, and need removal if activity is to be maintained; so that, pretty certainly, it might be anticipated that the brisker the effervescence the more rapid would be the dissolution of the zinc, in consequence of the more rapid conversion of the liquid, and the consequent change of contact. As a matter of fact, we find that, even when the temperature is equalised as far as possible, one solution of sulphuric acid is neutralised by zinc in rather *less* than the time taken by an equal volume of another solution of sulphuric acid, of only half the strength, acting upon the same extent of

zinc-surface, neutralisation being estimated by cessation of effervescence.

Thus it appears that the nascent hydrogen hypothesis is not only inadmissible, but is quite insufficient to explain the special activity of the mixed acids.

II. *As to Sulphuric Acid Hastening the Reduction of the Nitric Acid by the Zinc, by Decomposing Nitrates and thus keeping it Free.*—When nitric acid alone acts upon zinc, by far the greater part of it is converted to zinc nitrate, and a little to ammonium nitrate. By decomposing these salts, and thus leaving the unreduced nitric acid free, sulphuric acid will undoubtedly hasten, to a certain extent, the reduction of the nitric acid, and, since nitric acid is more active towards zinc than its equivalent of sulphuric acid, will also hasten the dissolution of the zinc. But the experiments described show clearly the insufficiency of this action of the sulphuric acid; for in them nitric acid has been present in such abundance as to render the small quantity of it fixed as nitrate of no practical account. And, besides, the mixture which has proved so active contained in a given volume only a fourth of the nitric acid present in the much less active solution of this acid by itself.

The hypothesis advanced by Deville, and maintained by one of us in a previous paper, that the acids, when mixed, act upon zinc just as if they were not mixed, cannot, therefore, be accepted as sufficient to explain the special power of the mixture, although it is partly true. The evolution of hydrogen by the mixture shows that the sulphuric acid exerts at least to some extent its proper action upon the zinc. The formation of ammonia, from the first moment of the reaction, shows that the nitric acid also exerts its proper action, as we shall endeavour to establish in a later section, and by further evidence which we hope to give in a forthcoming paper.

III. *As to Sulphuric Acid Acting upon the Zinc so as to make it more Active towards the Nitric Acid.*—As the action of an acid upon zinc proceeds, it becomes accelerated by the increasing galvanic differentiation of the surface of the metal; but the effect of nitric acid in increasing the activity of the zinc towards fresh portions of the acid, appears to be much greater than that of sulphuric acid, and we, therefore, think that the effect of sulphuric acid in this way is quite unimportant.

IV. *As to Nitric Acid Acting upon the Zinc so as to make it more Active towards the Sulphuric Acid.*—In order to test the relative power of nitric acid in developing in zinc activity towards sulphuric acid, we have immersed for five minutes sheets of zinc, cut and cleaned as for our other experiments, in 2400 c.c. each of 5 per cent. nitric acid, and have then submitted them to the action of 15 per cent. sulphuric

acid. Of two sheets immersed, one in 5 per cent. nitric acid and one in 15 per cent. sulphuric acid, the former lost in five minutes 2.68 grams, the latter 0.15 gram; then immersed for a second five minutes, both in 15 per cent. sulphuric acid in separate vessels; the former lost 1.12 grams and the latter 0.99 gram. The experiment was repeated with fresh materials. A sheet five minutes in 5 per cent. nitric acid lost 2.71 grams, and another in 15 per cent. sulphuric acid lost 0.23 gram. Again immersed, this time both in 15 per cent. sulphuric acid, the former lost 1.38 gram, and the latter 1.00 gram.

The advantage thus lay with the nitric acid preparation, but not to any great extent, and this advantage seems to be more than accounted for by the much greater extent to which the zinc had been corroded by the nitric acid than by the sulphuric acid.

As in the mixed acids the concentration of the nitric acid was only a fourth of what it was in these experiments, its greater corroding effect should have been unimportant when thus reduced. This explanation of the wonderfully high activity of the mixture seems therefore to be insufficient.

V. *As to Sulphuric Acid Intensifying the Action between the Zinc and the Nitric Acid, by Acting upon the Nitric Acid and Combining with it.*—By regarding nitric acid as ammonia, with oxygen and hydroxyl replacing its hydrogen, we may conceive of sulphuric acid forming a salt with it, as it does with nitrosyl. But as there is no evident reason why such a salt should be more active towards zinc than free nitric acid, it is useless to speculate further in this direction.

VI. *As to Nitric Acid Intensifying the Action between the Zinc and the Sulphuric Acid by Acting Directly upon the Sulphuric Acid.*—This hypothesis we discuss and uphold in the next section.

Nitric Acid and Zinc Exert a Specific Combined Action upon Sulphuric Acid.

There seems to us but one explanation which fully accounts for the specially great activity upon zinc of a mixture of nitric and sulphuric acids, and that is, that *the sulphuric acid, perhaps inactive to zinc alone (if pure), and certainly inactive towards nitric acid alone, is freely decomposed by contact with the two at once*, its hydrogen going to the nitric acid, and its sulphate radical going to the zinc. Just as neither stannous chloride nor nitric oxide can alone decompose hydrochloric acid, while together they do so without difficulty, so together nitric acid and zinc act freely upon sulphuric acid, although apart they may have little or no action upon it. There will always, indeed, be some little action between the zinc and sulphuric acid only, and much probably between the nitric acid and the zinc, but these actions are independent

of and accidental to the specific action of the zinc and nitric acids upon the sulphuric acid, with which they are concurrent.

There must, of course, be a like specific action of tin and nitric acid upon sulphuric acid or upon hydrochloric acid, and in this case, whereas the combined action is very great, the separate actions, particularly that of the sulphuric or hydrochloric acid upon the tin, are very slight. Again, there is the specific action, pointed out in another paper (this Journal, 45, 194), of a mixture of selenium and cold sulphuric acid upon hydrochloric acid, in which the chlorine of this acid goes to the selenium and the hydrogen to the sulphuric acid, which it reduces.

That the theory here advanced is quite adequate to explain the rapid action of the mixed acids upon zinc, is evident. That it may well account for the production in the mixture of hydroxyamine, only found in traces when nitric acid alone acts on zinc, must be equally admitted. The trace of hydroxyamine found when only nitric acid is used, may well be due to the presence of traces of other acids, and then the specific action of the mixture becomes sharply differentiated by its products from the separate action of the zinc upon the nitric acid.*

It need hardly be added that this theory applies to all changes commonly treated as the effects of nascent hydrogen, and that, in all of them, therefore, it is held that the reductions effected are unconnected with the production of free hydrogen. Hitherto the power of the zinc-tin class of metals to act like stannous and ferrous salts as hydrogenising agents, although with greater intensity, has been passed over unnoticed, because of the additional power they possess of actually liberating hydrogen. But the facts, as now ascertained by us, require that the two modes of action by these metals should be admitted as distinct.

Nascent hydrogen is an imaginary reagent only.

Without pretending to be able to give any precise explanation of the peculiarity and different power of different hydrogenising mixtures, of which a metal is a part, we consider that the theory here propounded makes these peculiarities and different powers more intelligible than they are on the nascent hydrogen hypothesis. Thus, that nitrobenzene gives the *base*, aniline, to an *acid* reducing mixture, and not to a basic mixture such as sodium and water; that the *base*, hydroxyamine, is formed in *acid* mixtures, and the *acid*, hyponitrous acid, in *basic* mixtures, seem natural events when we regard the substances in the mixture as exerting their characteristic influence, whereas, considered as the varying effects of the contact of nascent

* For additional remarks on this point, refer to the next section but one after this.

hydrogen, they seem inexplicable, unless we assume that such nascent hydrogen bears upon itself in each case the marks of its origin.

There is one point in the view here taken of the nature of the reduction of nitric acid by sulphuric acid and zinc, which needs consideration, and that is the liberation of free hydrogen which takes place, even when the sulphuric acid is not in undue quantity. Could nitric acid be completely changed into hydroxyamine by this reaction, just seven equivalents of sulphuric acid would be required, six being for the zinc and one for the hydroxyamine. But with such a proportion of the sulphuric acid hydrogen is freely liberated. The explanation appears clearly to be this: much, even half, of the nitric acid in contact with the zinc at any moment attacks the zinc direct, leaving for the instant a corresponding part of the sulphuric acid touching zinc in absence of nitric acid; this part of the sulphuric acid partly attacks the zinc and yields free hydrogen, and partly, principally no doubt, attacks the zinc nitrate, reproducing nitric acid. Thus, the separate action of the nitric acid upon the zinc brings about a certain degree of the action of the sulphuric acid alone upon the zinc.

Hydroxyamine in Acid Solution is not Reducible by Zinc.

In the paper "On the Production of Hydroxylamine from Nitric Acid," tabulated results are given, from which it can be seen that, on leaving a mixture of nitric acid and either sulphuric or hydrochloric acid upon zinc, hydroxyamine is both produced and destroyed. In the course of many experiments since made, we have further observed, in the first place, that a sufficient excess of sulphuric acid being used, that is, ten equivalents or more to one of nitric acid, the maximum amount of hydroxyamine, when reached, remains unchanged for several minutes longer, and, in the second place, that its amount only begins to diminish when the sulphuric acid has become much neutralised. We give a few examples of our testings in illustration of this.

Zinc 36 grams, nitric acid 1 gram, sulphuric acid 60 equivalents (to 1 nitric acid) or 47 grams, dilution to 400 c.c., temperature $11\frac{1}{2}$ —53°; at 9, 13, and 17 minutes there was always the same quantity of hydroxyamine found present, equivalent to 0.45 gram nitric acid.

Zinc 18 grams, nitric acid 1 gram, sulphuric acid 15 equivalents, dilution to 200 c.c., temperature 9—34°; at 13, 15, and 17 minutes there was the same quantity of hydroxyamine found, also equivalent to 0.45 gram nitric acid.

Zinc 36 grams, nitric acid 1 gram, sulphuric acid 15 equivalents, dilution to 400 c.c., temperature 9—25°; at 16, 18, 20, and 22 minutes

there was found the same quantity of hydroxyamine, equivalent to 0.42 gram nitric acid.

These are some of the experiments performed with one kind of zinc, rather weak as a means of producing hydroxyamine (see the next section but one to this). With more productive zinc the steadiness of the quantity of hydroxyamine is less prolonged.

It is hardly necessary to give fresh examples of the other point observed, namely, the descent in the quantity of hydroxyamine as the time when effervescence ceases is approached and passed, because many were given in the other paper. We give here therefore, just one out of many more.

Zinc 36 grams, nitric acid 1 gram, sulphuric acid 10 equivalents, dilution to 200 c.c., effervescence ceasing at 13 minutes; the hydroxyamine found at 10, 13, 17½, and 32 minutes was successively equivalent to 0.48, 0.44, 0.36, and 0.26 gram nitric acid.

An explanation of the steadiness of the quantity of hydroxyamine for some minutes, readily *presented* itself, being that hydroxyamine was undergoing destruction at the same rate as nitric acid was being converted into it. But we found that, although traces of nitric acid lingered on afterwards, almost all of it had disappeared by the time that the hydroxyamine reached its maximum amount, and this seemed to show that hydroxyamine was stable for a time in the solution. Decisive testing was not, however, easy, where it was a question of the presence of a very small fraction of a gram of nitric acid (that of a trace being certain) in several hundred cubic centimetres of solution.

The matter was easily settled in another way. To dilute sulphuric acid standing over granulated zinc, a solution of hydroxyammonium chloride of known strength was added and then, after a time, the zinc sulphate solution was titrated for hydroxyamine. In this way it was first found that hydroxyamine could exist for a time with sulphuric acid and zinc without change, and then that by keeping up active effervescence through the occasional addition of acid, hydroxyamine could be left for any reasonable time in such a solution without material change.

In one experiment, of a solution of hydroxyammonium chloride 10 c.c., containing 0.033 gram of hydroxyamine, were made up to 100 c.c. with water, containing a little sulphuric acid. The mixture was poured upon 45 grams of granulated zinc, and thus exposed to a relatively very large surface of zinc. It was left in contact with the zinc for two hours, dilute sulphuric acid being occasionally added, so as to keep up effervescence. The solution, still effervescing, was poured off, and titrated for hydroxyamine, and the whole of this was found unchanged. Indeed, the anomaly was observed, of a little more iodine being required than equalled the whole hydroxyamine. But we

find that, in presence of a concentrated solution of zinc salt, a clear excess of iodine solution is decolorised over that calculated for the hydroxyamine.

We then tried the action of zinc alone upon a dilute solution of hydroxyammonium chloride. Here there was a marked destruction of the hydroxyamine in two hours, one-eighth to one-fourth disappearing. The nitrate appeared to be somewhat more unstable. Acidified with a little sulphuric acid, however, the nitrate gave in ten minutes on zinc, a third *more* hydroxyamine than it contained in consequence of the conversion of part of its nitric acid to that base. (The nitrate consists by weight of one part base to two parts acid, so that about a third of its acid became hydroxyamine.) The presence of zinc sulphate or ammonium chloride or of free ammonia, appears to be without marked effect.

Hydroxyamine is thus seen to be only very slowly decomposed by the contact of zinc with its cold solution, even in absence of acid. It was otherwise, however, in the case of hot solutions, for in these the hydroxyamine is destroyed by zinc with relative rapidity, although still wonderfully resistant to decomposition. Boiled for a quarter of an hour in 100 c.c., and less, of solution, upon 35 grams of zinc, 0.033 gram was reduced to 0.02 gram. Heated to 70—80° for one hour upon 35 grams of zinc, 0.033 gram hydroxyamine in 100 c.c. was reduced to 0.008 gram.

The observed rise, the continuance for a time at a level, and then the decline of the quantity of hydroxyamine, during the reduction of nitric acid by zinc and another acid, are due, therefore, to the nitric acid being partly converted to hydroxyamine during the rise, to the hydroxyamine being stable in an acid solution in contact with zinc, and to its being gradually destroyed when in hot solution by contact with zinc, if no free acid is present. The beginning of its destruction before all the acid is neutralised may be safely attributed to neutralisation having existence close to the zinc, while the body of the solution is still acid. Another point to be explained is that the destruction of the hydroxyamine, in these experiments upon the reduction of nitric acid, is somewhat greater than might be expected from the results obtained with previously prepared hydroxyammonium chloride. There is no difficulty, we consider, in believing this to be due to the "active" condition of the zinc, induced by the previous extensive action of the acids upon it, which leaves it blackened and much corroded. In the direct experiment upon hydroxyamine in absence of acid, the zinc is but little affected, and preserves much of its initial activity.

Ammonia and Hydroxyamine appear to be not Consecutive Products, but Products of Parallel and Independent Reductions.

As pointed out in the previous paper, ammonia is abundant from the first, during the reduction of nitric acid by sulphuric acid and zinc. Its non-production from hydroxyamine, in the presence, that is, of free acid, gives its appearance during this reduction a new interest. Nitrous oxide is also produced. We have made no attempt to estimate the very small quantities of this gas formed in our experiments. Deville's determinations may be referred to on this point, but we ourselves in Japan have no means of doing so, for purposes of illustration.

A few determinations only of ammonia have been made by us, and further work in this direction is desirable. Having poured off the acid solution from the zinc at those times when it was calculated that the hydroxyamine would have just reached its maximum, one part was titrated for hydroxyamine, and another titrated for ammonia, by adding first sodium carbonate until some zinc carbonate was precipitated, then iodine to destroy hydroxyamine, then precipitating nearly all the zinc by sodium sulphide, and distilling the mother-liquor with potassium hydroxide. The ammonia was received in acid and titrated. In this way we obtained ammonia equivalent to much of the nitric acid not convertible into hydroxyamine.

By using a very great excess of sulphuric acid nearly, if not all, the nitric acid unconverted to hydroxyamine appears to be converted into ammonia. This is in accordance with Kinnear's (*Chem. News*, **46**, 63) results, and we believe it be correct, but there is difficulty in determining closely a very small quantity of ammonia in presence of very much zinc salt, and, without more trials than we have made, we cannot assert that it is so.

Under favourable conditions, we have got as much as, and even more than, seven-tenths of the nitric acid converted to hydroxyamine, but, with unsuitable zinc, we have sometimes failed to get more than two-tenths converted. In our former paper, we mentioned a yield of eight-tenths of the nitric acid as hydroxyamine, but we were not confident as to this yield having been really obtained.

In a preceding section, we have attributed the production of hydroxyamine entirely to the specific action of the zinc and the nitric acid upon sulphuric acid. We can now almost assert that ammonia is not a product of that specific action, and that the ammonia, freely produced from the first during the dissolution of the zinc in the mixed acids, is formed solely by the direct action of the nitric acid upon the zinc. Uncertainty thus seems cleared away as to the specific hydrogenising action of the sulphuric acid upon the nitric acid. For,

although nitric acid in contact with zinc and water can readily hydrogenise itself without the aid of any other acid, the product is then ammonia, not hydroxyamine, whereas when nitric acid is hydrogenised by sulphuric acid, the product is hydroxyamine and not ammonia.*

In the paper on the production of hydroxyamine from nitric acid, we have said that a perfect metal for making hydroxyamine would be one active towards dilute nitric acid, inactive towards sulphuric or hydrochloric acid, and inactive towards hydroxyamine. With our present knowledge we would alter this, and say, that such a metal should be inactive to nitric acid alone, and active only to a mixture of nitric acid with either hydrochloric or sulphuric acid. The above considerations at once explain why it is that a metal may freely produce ammonia from nitric acid and yet produce hydroxyamine from it only with difficulty, or not at all. For, in such cases, there may be strong action of the metal upon nitric acid, or independently upon both acids, whereby ammonia will be formed, and yet be no specific action upon the two acids combined, which would give rise to hydroxyamine. Or again, the effect of this specific action may be as nothing compared with that of the superior activity of the metal towards the independent acids.

Dependence of the Yield of Hydroxyamine upon undetermined Peculiarities in the Nature of the Zinc Used.

Granulated zinc may differ widely in its power of yielding hydroxyamine, but a given preparation of it, or mixtures of similar preparations, will show under the same circumstances the same power at one time that it has shown at another. The differences observed in this relation between different preparations of granulated zinc, depend in part upon the nature of the zinc melted down, of course, but they also depend upon differences in the process of granulating. Partly, no doubt, in consequence of the fact that apparently both the condition of the zinc before it has been granulated, and the character of the operation of granulating it, may exert marked influence upon its power to produce hydroxyamine from nitric acid, but at any rate

* In our first paper we have said—in support of the view that the reduction of hydroxyamine to ammonia by zinc is due to the metal uniting with the hydroxyamine to form zinc ammonium hydroxide—that such a compound as zinc ammonium hydroxide actually occurs in the hot alkaline solution resulting from the action of hydrochloric and nitric acids upon zinc, and slowly decomposes into ammonia and zinc hydroxide. We would now point out that this soluble alkaline compound may be hydroxychloride of zinc, $\text{HO}\cdot\text{Zn}\cdot\text{Cl}$, produced by the action of hot solution of zinc chloride upon zinc, and therefore the union of zinc with hydroxyamine is as yet hypothetical.

we have failed in the attempts we have made to secure at will granulated zinc of a uniform and high power in this respect, or to ascertain any sufficient knowledge of the causes of its varying power.

On one occasion, there seemed to us to be a marked difference between the same zinc when granulated at different temperatures. By running the zinc when almost boiling hot, and then again, from the same melting, after the zinc had cooled almost to the solidifying point, a much more productive lot of granules was obtained from the second running than from the first. But on trying the effect of this difference in operating again and again, we got no confirmation of our first result. We also varied the process by pouring from a height, and pouring near the water, and of granulating in boiling water and granulating in cold water, but from all our trials we learnt nothing. At one spell of work we could repeatedly granulate zinc turning out to be of nearly equal power, but on another occasion we could not count on producing more zinc of the same power.

Effect of Iron in the Zinc.—It is no doubt impossible to melt zinc in an iron vessel without getting iron dissolved in it, but, with precautions, the quantity may be made so small as to be insignificant if not inappreciable.*

Iron in zinc appears to act injuriously, judging from our experiments. Zinc which had taken up iron by being melted in a wrought-iron pot at a high temperature, had its power to produce hydroxyamine reduced by half. But even zinc from the same stock, but of different granulations, sometimes showed considerable differences without any corresponding differences in iron-content.

Some granulated zinc, which would not give us a greater proportion of nitric acid converted to hydroxyamine than three-tenths, was found to contain as much as 0.67 per cent. of iron, but then a zinc-iron alloy from a galvanising tank, and containing *several units per cent.* of iron,† gave more than two-tenths of the nitric acid as hydroxyamine, and,

* *Note on Granulating Zinc.*—If, as is commonly the case in a chemical laboratory, the zinc is melted in an open wrought-iron ladle coated with black or red oxide, and the temperature allowed to run high, much iron may enter the zinc, which is not surprising. It is nearly certain, for one thing, that iron oxide is readily reduced by melted zinc and dissolved more readily than is the massive iron of the pot. Further, it is well known in galvanising, that wrought iron becomes rapidly dissolved by liquid zinc, and that, therefore, cast iron must be used for the vessels. Zinc rapidly takes up iron from a clay crucible, when heated in it. But we have found that, when a cast iron deep pot is used, scoured clean inside and well black-leaded, and that the pot is kept covered, and is heated on a smart fire until the zinc is only just melted, the zinc can be poured from the pot leaving this clean and with the coating of black-lead almost intact, and carrying with it no iron beyond that already contained in it.

† Analysed by us, but record mislaid.

still more remarkably, a zinc containing only about 0.1 per cent. of iron has given us as low a maximum yield of hydroxyamine as that which contained 0.67 per cent. iron.*

Lead.—We melted lead with the zinc in varying small proportions before granulating, and obtained quantities of hydroxyamine with these plumbiferous zincs, which showed no relation to the quantities of lead. One batch of metal containing $2\frac{1}{2}$ per cent. of lead actually gave us some of our best yields (six-tenths of the nitric acid converted to hydroxyamine), but other preparations with about this proportion of lead quite failed to give particularly high yields. Zinc saturated with lead gave low yields, but this fact was due perhaps to the effect of the presence of the lead in lessening the surface of the zinc exposed. We arrived at the conclusion that a little lead had no appreciable influence.

Freshly amalgamated zinc is insensible to the specific action of the mixed acids, so that the action of dilute nitric acid in dissolving such zinc, which is much less than upon zinc without mercury, is not sensibly increased by the presence of sulphuric acid, and hydroxyamine is not formed. At least this is the case for some time, but gradually, under the action of nitric acid, the amalgamation ceases to protect the zinc against the sulphuric acid, and then it dissolves faster, and hydroxyamine is formed. The fact here described is further evidence of the insufficiency of the view that sulphuric acid modifies the action of nitric acid merely by decomposing its zinc salt as fast as it is formed.

When treating of the action of sulphuric acid upon zinc, we indicated the difficulties of carrying out experiments in such a way as to place the influence of each circumstance upon that action clearly and unmistakably in view. The difficulties become much greater when the investigation refers to the action of the mixed acids. The one among them which is possibly insurmountable in any case, and which is certainly so in the circumstances in which we find ourselves, is the fitful behaviour of ordinary zinc towards the mixed acids, if we may be allowed so to put what, plainly stated, is only our own inability to detect the causes of the diverse behaviour of different samples of zinc. We have not succeeded even in tracing any evident connection between the relative activity of zinc in sulphuric acid and its relative power of generating hydroxyamine from the mixed acids. For before the problem of doing so presented itself to us, we had used up what zinc we had that produced high yields of hydroxyamine,

* Did the iron of ferruginous zinc dissolve in the acid, its destructive activity upon hydroxyamine would be certain, but it is well known that, while zinc is abundantly present, iron does not dissolve in sulphuric acid, and in our experiments, although a little nitric acid was present, no iron was found in the solution.

and could not renew our stock. We can certainly say that a zinc may be very active in sulphuric acid, and yet prove a poor means of getting hydroxyamine. On the other hand, the zincs which gave us very high yields were such as very quickly dissolved in the mixed acids, but whether such zincs would also have been very active upon sulphuric acid alone we cannot say with certainty; all that we can say is that we think it probable they would.

We have, in consequence of this and other difficulties, been unable to carry out, even in part, an investigation which would serve to establish the exact relations existing between the action of sulphuric and nitric acids, and temperature, dilution, varying proportions of the acids, time, and other circumstances. But in our attempt at such an investigation, made for the most part before we had learned how much zinc may vary in its power, we had made observations concerning these relations which seem to be worth recording, although they are insufficient of themselves to establish anything with certainty. Without, therefore, describing in detail what we have done, and tabulating the results of our numerous experiments, we shall summarise such conclusions as we have arrived at.

The apparent Influence of Temperature, Time, Dilution, and other Conditions upon the Reaction between Zinc and Acids.

In hot solutions, hot even to boiling, not only does the action of acids upon the zinc proceed very much more quickly, but *the yield of hydroxyamine is increased*. In accordance, however, with what has already been said about the destruction by zinc of hydroxyamine in hot solution, it should be remembered that the solution must be preserved highly acid while in contact with the zinc. It is consequently not desirable to cool the mixture during reaction, as was indicated in our former paper, but only to guard against the rapid neutralisation of the acids which takes place when they have grown hot. The cause of the beneficial action of heat is probably an alteration in the relative energy of the acids upon zinc, in which case something further may yet be learned through this concerning the specific action of the mixed acids.

The time taken to neutralise a given quantity of an acid, or to complete some other chemical action upon it, such as the formation of hydroxyamine from nitric acid mixed with sulphuric acid, is directly as the dilution of the acid, and inversely as the area of contact between the metal and the solution, other circumstances being equal. It is independent of the quantity of the acid.

It will not be doubted that if in a given volume of a certain dilute acid twice the surface of zinc is exposed in one case that is exposed

in another, the rate of neutralisation with twice the zinc will be twice as great. In practice, however, there are modifying circumstances. Thus, the heating is greater with the larger surface of zinc, and therefore that does its work somewhat more than twice as fast as the smaller surface. Again, twice the weight of granulated zinc of one quality may be considered to expose twice the surface, but in practice it does not always act twice as fast. The reason is this: there are to be considered, in making the comparison, the free surface of the heaps of granules, and the surface of the interstices of the heaps and the cavities of the granules, for the surface of the heaps more rapidly changes contact with the liquid than do the interior surfaces. Now, since the upper surfaces of the heaps in the flasks will be more nearly equal to each other than in the ratio of 2 : 1, it follows that twice the weight of granulated zinc will not be twice as active, except perhaps with violent shaking or violent effervescence. With dilute solutions, twice the weight of granulated zinc was found not able to produce hydroxyamine twice as fast; but with more concentrated solutions it appears to be so, probably because of more violent effervescence, and of shortening of the time required, since differences in rate of action would then be less measureable.

But another remarkable circumstance was observed by us. Using twice as much zinc we generally got a somewhat worse yield of hydroxyamine. If we consider that in the deeper recesses of the heap a little local neutralisation of the acid, with consequent destruction of hydroxyamine, occurred, we have a reason why the deeper heap of granules should unfavourably compare with the other, else it is difficult to conceive how there could have been any difference, and that observed must be referred to errors of experiment. But in several pairs of experiments we got this difference, which was that between 44 and 42, in another case that between 47 and 45, and in a third case, with less dilution of acid, 45 and 44. At any rate, one explanation serves, when the quantity of granulated zinc is doubled, both for the lower yield of hydroxyamine and for the rate of action being slower than that calculated. When the acid is sulphuric acid, its action is certainly not proportionate to its degree of dilution; this we have fully shown in an earlier section.

This fact, however, is sufficiently accounted for by the changing condition of the zinc, galvanic or otherwise, during the action of the acid. With the mixed acids, as well as with nitric acid alone, the proportionate action proves to be so far true on trial as to justify us in believing that it would be strictly so under parallel circumstances. Thus, given a certain quantity of granulated zinc, it was always approximately true in our experiments that double the volume of dilute acids took double the time to reach its maximum content of hydroxy-

amine, or double the time to cease to effervesce, provided shaking the vessels was kept up with practical uniformity.

We have also stated that the time taken to effect a given change is independent of the quantity of the acid, that is, independent of its concentration, within the limits of the occurrence of a common reaction. This proposition seems worthy of separate consideration, although it is but a corollary to that as to the time being proportionate to the volume. It is only experimentally true, or approximately true, when the acid is either nitric acid or the mixed acids. When we poured upon a certain quantity of zinc a certain volume of dilute mixed acids of double the concentration of other mixed acids, both the highest yield of hydroxyamine to be got and the termination of the effervescence were reached in nearly the same time in one solution as they severally were in the other. There was, however, generally a little difference in favour of the stronger solution, in consequence no doubt of the greater rise in temperature.

It is easy to see that, although the completion of a given reaction, such as the neutralisation of the acids or the reduction of all the nitric acid, will take a time dependent only on the dilution and the surface of the zinc, yet the reaction will not proceed to its completion at the same *rate*. We have scarcely any experimental evidence on this point, but then we have not specially worked for it. The argument is this. Taking as the simplest case that of equal concentration but different volume, it must be that the greater volume will proceed for a time faster to saturation or reduction than the other. For, starting at the same rate of action, because of equal concentration, the greater volume must necessarily diminish in concentration, by equal rate of action, less rapidly than the smaller volume, and soon, therefore, as being the stronger solution, act on the zinc more powerfully than the other. During the latter part of the action, this state of things must be reversed.

There is a consideration in connection with the rates of action of dilute acids upon zinc which bears upon the theory of the specific action of mixed nitric and sulphuric acids. Suppose that zinc were not partly passive towards sulphuric acid, or at least less active towards it than towards nitric acid, then, no matter in what proportion we mixed the acids in a solution, the two ought to get entirely neutralised or decomposed together. But, the sulphuric acid being in sufficient quantity, this does not prove to be the case, more or less of this acid remaining after all nitric acid has disappeared. And yet the mixed acids possess an activity that rivals that of nitric acid itself. Plainly, then, the part played by the nitric acid is not mainly that of acting on the zinc, so as to render it more sensitive to the sulphuric acid than it was, and that part of the sulphuric acid which does not

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act specifically with the nitric acid has still to get neutralised in its own slow way.

Another point for consideration is the divided activity of the nitric acid, this acid acting in part directly upon the zinc to form ammonia, even in presence of excess of sulphuric acid, and in part in conjunction with the sulphuric acid to form hydroxyamine. It would seem to follow from this that nitric acid by itself has an activity towards zinc superior to that of the mixed acids, and in consequence acts to some extent directly upon the zinc.

Time of Maximum Yield of Hydroxyamine.—The want of a knowledge when to look for the moment of highest production of hydroxyamine, was a considerable hindrance to satisfactory working. In a further series of experiments we should not feel this difficulty, because we now know that by keeping up free effervescence by adding some more sulphuric acid we need not fear destruction of hydroxyamine to a material extent.

The main circumstances determining the time necessary for reduction of all nitric acid, are the dilution of the nitric acid, the surface of the zinc, and the temperature. Besides may be mentioned the degree of agitation of the liquid through shaking the containing vessel and through the effervescence caused by the sulphuric acid. A greater excess of sulphuric acid somewhat quickens the reduction of the nitric acid, but a sufficient reason for this appears to exist in the more violent effervescence and consequent motion of the liquid, and in the greater rise in temperature.

The Yield of Hydroxyamine is not affected by the Quantity of Sulphuric Acid in excess, but is affected by its Degree of Dilution.—In our former paper on the production of hydroxyamine from nitric acid, we have shown that as the proportion of sulphuric acid is increased from 3 equivalents to 11, so is the proportion of nitric acid converted to hydroxyamine increased. We have since tried the effects of larger proportions still of sulphuric acid. When there is about 1 gram of nitric acid in 200 c.c. of solution, an increase above 14 or 15 equivalents of sulphuric acid appears to have little effect; but when the nitric acid is twice as dilute as this it proves advantageous to increase the sulphuric acid to 20—25 equivalents. Or, to put the matter in another form, the sulphuric acid should be in quantity not less than 5—6 grams in every 100 c.c., and need not be more, unless the quantity of nitric acid should exceed 0.7 gram in the 100 c.c. These proportions are somewhat affected by the quality and quantity of the zinc employed, zinc capable of giving high yields of hydroxyamine appearing to require a somewhat less concentrated sulphuric acid than zinc giving low yields.

Beyond, then, a moderate limit, such as the above, an increase of

sulphuric acid has no effect on the yield of hydroxyamine. Were there only the specific action of the two acids together upon the zinc taking place, just seven equivalents of sulphuric acid would be required. The direct action of the nitric acid upon the zinc would but little affect the quantity of sulphuric acid needed, since the indirect exhaustion of the sulphuric acid through the nitric acid becoming ammonia and nitrous oxide is almost the same as its direct exhaustion in converting the nitric acid to hydroxyamine. But, as we have already said, the direct action of the nitric acid upon the zinc leaves some of the sulphuric acid free to divide itself between zinc nitrate and metallic zinc, with the latter of which it exhausts itself without any effect, direct or indirect, in hydrogenising nitric acid, but evolves hydrogen instead. Now to what an extent the proportion of seven equivalents of sulphuric acid should on this account be exceeded, or even whether it need be exceeded at all, will depend upon the nature of the zinc. For another purpose, however, an excess of sulphuric acid is desirable, and that is to keep the solution a little acid to the end of the reaction with the nitric acid, and still a little longer, in order to guard against destruction of hydroxyamine by zinc.
