VIII.—COMMUNICATIONS FROM THE LABORATORY OF THE LONDON INSTITUTION.

Researches on the Reduction of Nitric Acid and the Oxides of Nitrogen. Part I. On the Gases Evolved by the Action of Metals on Nitric Acid.*

By J. J. ACWORTH and HENRY E. ARMSTRONG, F.R.S.

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* The substance of this paper was communicated to the Society on June 30th, 1876, and the experiments described in it were made previous to this date.

§ I. Introductory.—Although it is a generally recognised fact that the composition of the gases evolved when metals are dissolved in nitric acid depends not only on the metal employed, but also on the strength of the acid and the temperature at which the reaction takes place, no sufficient examination of the influence of these various factors on the nature of the gaseous product has ever been made: and what is even more remarkable, no quantitative determination of the amount of gas produced by the dissolution of a given weight of any metal in acid of a certain strength appears to have been attempted.

It is not easy to understand how so important a problem as that of the action of metals on nitric acid should have so long been regarded, we may almost say, with complete apathy by chemists. Doubtless the difficulty of collecting the gaseous product without loss and in a pure state, and of analysing the somewhat complex mixtures obtained-difficulties which are now entirely removed by the invention of those most important engines of research, the Sprengel-pump and the gas-analysis apparatus-has in part contributed to this; probably, however, it is chiefly attributable to the influence of the dogmatic teaching to which we have long been subject in these matters: for in scarcely any of our text-books is the least attempt made to explain the changes which result in the formation of the various oxides of nitrogen and of nitrogen itself. We find merely the statement that they are the products of the more or less complete deoxidation of the acid, and a single equation is invariably used to express that which undoubtedly involves a series of changes, and should therefore be represented by a series of equations; indeed, as a rule, explanatory equations are conspicuous by their absence from our text-books, and hence one of the most effective means of awakening a desire in the student to analyse the phenomena brought under his notice remains undeveloped.

same time decomposes water, the hydrogen of which then combines with the nitrogen of the acid-into ammonia. Which of the above products is formed depends partly on the affinity of the metal for oxygen, partly on the temperature and concentration of the acid."

The explanation herein contained, although perfectly sufficient as long as the older theory of the nature of acids and of the formation of salts prevailed, ceased to be so when the acids came to be regarded as hydrogenised compounds ("bydrogen salts"); nevertheless, the language used in most chemical works, even at the present day, is almost invariably such as to lead the reader to attribute the reduction which nitric acid undergoes when acted upon by metals, to the metal itself, whereas it can scarcely be doubted that it is due, not to the direct action of the metal, but to the action of the hydrogen displaced from the acid by the metal. Miller's Elements of Chemistry (5th ed., 1874, vol. ii, p. 154), however, is the only text-book in which it is to our knowledge that this latter explanation is given.

§ II. Theory of the Formation of the various Products obtained on dissolving Metals in Nitric Acid.-From what is already known on the subject, and from our own experiments, we believe the following to be the most consistent and probable explanation which can be given of the formation of the gaseous and other products obtained by dissolving various metals in nitric acid.

We regard the action of the metal as consisting simply in the displacement of the hydrogen of the acid and the formation of the corresponding nitrate in the manner expressed by the following equation, in which R denotes the amount of any metal which is equivalent in combining or displacing power to two atoms of hydrogen:

1.
$$R + 2HNO_3 = R(NO_3)_2 + 2H.$$

Under no circumstances, however, is the hydrogen thus displaced evolved as such; it at once acts on the free acid present (and even, in some cases, as we shall show later on, also on the metallic nitrate which has been formed), reducing it more or less completely to nitrous acid, nitrosidic acid,* hydroxylamine, or ammonia, as shown by the following equations:

> 2. $HNO_3 + 2H = HNO_2 + OH_2$. 3. $HNO_3 + 4H = HNO + OH_2$. 4. $HNO_3 + 6H = NH_2(OH) + 20 H_1$ 5. $NHO_3 + 8H = NH_3 + 3OH_2$.

* We employ this name to designate the acid-if, indeed, it be an acid-the salts of which were first described by Divers in 1870 (Roy. Soc. Proc., p. 425), in preference to that of hyponitrous acid, as it may be regarded as a compound of nitrosyl (NO) with hydrogen.

The gases which are evolved on dissolving metals in nitric acid result, we believe, from the decomposition of these reduction products and from their action upon each other.

The nitric oxide is chiefly, if not entirely, formed by the decomposition of the nitrous acid, in accordance with the equation :

6. $3 \text{HNO}_2 = 2 \text{NO} + \text{HNO}_3 + \text{OH}_2$.

We say chiefly, if not entirely, as it is possible that some nitric oxide may be produced from the nitrosidic acid since, according to Divers, although silver nitroside (AgNO) is soluble in dilute nitric acid without immediate decomposition, it is immediately oxidised by the concentrated acid, copious red fumes making their appearance; and moderately diluted nitric acid decomposes it with evolution of nitrogen, and production of apparently both nitrous and nitric acids in the solution. It is also possible that hydroxylamine may furnish nitric oxide on oxidation with nitric acid.

The nitrous oxide is in all probability chiefly the product of two distinct changes, viz., a, of the spontaneous decomposition of nitrosidic acid, which, as Divers has shown, breaks up with the greatest readiness into nitrous oxide and water; thus:

7.
$$2HNO = N_2O + OH_2$$
;

and b, of the action of nitrous acid on hydroxylamine, which, as V. Meyer has shown, takes place in the following manner:

8.
$$NH_2(OH) + HNO_2 = N_2O + 2OH_2$$
.

Finally, we regard the nitrogen as chiefly the product of the action of the nitrous acid on ammonia :

9.
$$NH_3 + HNO_2 = N_2 + 2OH_2$$
,

but it is *perhaps* in some cases in part, and in others entirely, the product of the action of nitric acid on nitrosidic acid.

The explanation we have advanced cannot be regarded as complete until the action of the various reduction-products upon each other under all the conditions which can occur in practice has been rigorously investigated—a task of no slight difficulty and magnitude; but before undertaking this, it appeared desirable to gain more definite information as to the behaviour of various metals, and especially as to the quantitative relation which the amount of gas produced bears to the amount of metal dissolved.

§ III. Method of Experiment.—In all our experiments we have employed weighed quantities of metal, and before bringing the latter into contact with the acid, the air has been exhausted as completely as possible from the apparatus; we have then allowed the action to take

place, and have afterwards collected, not only the gas evolved spontaneously, but also that given off on repeatedly heating the nitric acid solution in a vacuum. The total quantity of gas obtained has always been measured, and its composition determined; in most cases the gas evolved during the dissolution of the metal and on subsequently exhausting previous to heating has been collected apart from that evolved on heating, and the two portions separately analysed; sometimes the gas has been pumped off at various intermediate stages of the operation and the several portions separately analysed. In this way much information has been obtained which is of value in the discussion of the sources of the gases evolved.

The apparatus employed in most of our experiments consisted of a glass flask formed by expanding the one end of a piece of half-inch tubing about 4 inches long into a bulb of about 25 c.c. capacity, at a short distance above which was blown on the side of the tube a small bulb or pocket for the reception of the metal, the acid being placed in the lower bulb. The flask was closed by a caoutchouc plug, through which passed a narrow glass tube, provided with a stop-cock, bent twice at right angles; by means of this tube the flask was connected with a U-tube filled with pieces of solid potassium hydroxide, the U-tube being in connection with the Sprengel-pump.

It was impossible with this apparatus to employ concentrated nitric acid on account of its action upon the caoutchouc-plug, and also on account of the metal becoming acted upon by the vapours of the acid before the exhaustion was complete. A more perfect form of apparatus was therefore devised, consisting of a flask similar to that just described, but having a ground-glass stopper through which passed the tube of a dropping funnel provided with a stop-cock. It is represented by the figure on p. 59.

Although it is not to be expected that with an arrangement of the kind described the ingress of air can be entirely prevented, we have found that if all the joints are kept covered with glycerin, the leakage is so slight in the case of the glass apparatus, that practically the result is uninfluenced thereby; but in the case of the simpler form of apparatus, there is undoubtedly an appreciable error introduced, in consequence, probably, of the diffusion of air through the caoutchoucplug.

In making an experiment, the weighed piece of metal (as a rule foil was used) was placed in the pocket of the flask, and the acid —of which 15 c.c. were usually employed—was either poured into the lower bulb of the flask or sucked into the dropping funnel; the various parts of the apparatus having been connected together, the Sprengelpump was set in action and the pumping continued until the exhaustion was judged sufficient, when the metal was tipped into the acid.

In most cases pumping was not re-commenced until the metal was entirely dissolved; it was then carried on as long as an appreciable amount of gas was delivered. The stop-cock in the tube connecting



the flask with the U-tube containing potassium hydroxide was now closed, and the bulb of the flask surrounded with water heated to about 50° — 60° ; after heating it in this manner for a few minutes, it was surrounded with cold water, and when cold the stop-cock was opened and the gases which had been evolved from the solution were pumped off. This alternate heating, cooling, and removal of the gases evolved was then several times repeated, until, in fact, the quantity of gas obtained was almost inappreciable—which was usually the case after the second or third heating.

The mixture of nitric oxide, nitrous oxide and nitrogen obtained was analysed in the usual manner: the nitric oxide being determined by the addition of an excess of oxygen in presence of potassium hydroxide solution and subsequent removal of the unabsorbed oxygen by means of pyrogallol; the nitrous acid by explosion with hydrogen. It was frequently necessary to add a known volume of oxygen with the hydrogen in order to secure an explosion when the mixture con-The excess of hydrogen remaining after sisted chiefly of nitrogen. the explosion was usually determined in order to check the determination of nitrous oxide. The analyses were almost invariably performed in duplicate. The results of the nitric oxide determinations were almost uniformly satisfactory, but the estimation of the nitrous oxide in the extremely small amount of gas frequently remaining after the removal of the nitric oxide was not always satisfactorily effected; no difficulty, however, was experienced in the analysis of mixtures relatively rich in nitrous oxide of which a fair amount was available for combustion.

§ IV. Mode of stating the Results.—In order to facilitate the comparison of the results obtained with various metals and under various conditions, they are exhibited in the form of tables, in which are given the weight of metal taken; the temperature of the acid at the commencement of the experiment; the strength of the acid, of which, unless otherwise stated, 15 c.c. were always employed; the number of c.c. of gas obtained; the percentage composition of the gas; and the number of c.c. of gas per unit-weight of metal, *i.e.*, the quantity of metal equivalent to 2 grams of hydrogen.

§ V. Action of Copper on Nitric Acid.—The results of our experiments on the action of copper on nitric acid of various strengths are exhibited in Tables I and II. In discussing these results it will be necessary to consider, a, the composition of the gas evolved with various strengths of acid, it being remembered that, unless otherwise stated, whatever the strength of the acid, the same number of c.c. (15) of liquid was always placed in the bulb of the flask; b, the influence of temperature on the composition of the gas, as to which, however, we have hitherto made very few experiments; c, the volume of gas measured at 0° C. and under a pressure of 760 mm. of mercury obtained per unit-weight of metal; and d, the alteration in the composition of the gas due to the presence of varying quantities of cupric nitrate.

If the results of the experiments with acid of strength 1:2 (Nos. IJI to X inclusive) are compared, it will be seen that on the whole the composition of the gas evolved is remarkably constant, from about

c.c. of gas cale. as NO per unit- weight of metal.	Theory = 14880 c.c.	8891	00421	50101		15508 14707 13189 9193 14267 10220
ht of	${ m N}_2.$	78		114		$120 \\ 191 \\ 120 \\ 120 \\ 241 \\ 156 \\ 74$
unit-weig] tal.	$N_2O.$	78		151		180 206 121 27 215 215 219
f gas per mei	NO.	8417		15007		14628 13522 12527 8316 13508 9390
C.C. 0	Total.	434 8574		15272		$\begin{array}{c} 14928\\ 13919\\ 12768\\ 8584\\ 13879\\ 9683\end{array}$
osition	${ m N}_2.$	35 ·7 191	.70 .80 .70 .71 .74	24.	68 90 90 90 90 90	$\begin{array}{c} 1 & 80 \\ 1 & 93 \\ 2 & 81 \\ 1 & 12 \\ 75 \end{array}$
tage comp of gas.	$N_2O.$	10 ·3 ·92	$\begin{array}{c} 1 \cdot 33 \\ \cdot 87 \\ 1 \cdot 45 \\ 1 \cdot 21 \\ 1 \cdot 21 \\ \end{array}$	66.	1.69 1.47 1.55 1.64	1 ·21 1 ·55 95 30 2 ·27 2 ·27
Percen	NO.	54 •0 98 •17	97 '97 98 '33 98 '01 99 '26	98 .26	$\begin{array}{c} 97.63\\ 97.82\\ 97.54\\ 97.84\\ 99.10\\ 99.10 \end{array}$	97 -99 97 -15 98 -12 96 -89 97 -33 96 -98
c.c. of gas	obtained.	2 ·4 43 •48	5 2 •2 2 42 •22 43 •28 42 •01 41 •90	221•63	47 •16 40 •41 42 •67 40 •73 45 •18	216 15 201 • 99 79 • 55 20 • 65 33 • 10 22 • 91
Strength of acid	used.	1:0 1:1		1:2		NNNNNN
E		15°		13°		10° 11° 11° 8° 50°
Weight of metal	taken.	·35 ·3215		.920		918 920 1595 1525 150
No. of	expr.	I		ш		IV VI VI VI VI VI VI

I. Action of Copper on Nitric Acid.

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NITRIC ACID.

				-			-					
Weight of metal T.	Ę		Strength of acid	e.c. of gas	Porcent	tage comp of gas.	osition	0.0. 0	f gas per met	unit-weig al.	ht of	c.c. of gas calc. as NO per unit- weight of metal.
taken.			used.	obtained.	NO.	$N_2O.$	$\mathbf{N}_{2^{*}}$	Total.	NO.	N ₂ 0.	N_2 .	Theory = 14880 c.c.
.2285 90°	90		1:2	51.40	97 ·23	1.82	-95	14261	13866	259	136	15009
				46 :53 16 ·74	93 -68 95 -93	$\frac{4}{1} \cdot \frac{4}{18}$	$\frac{1}{2}.89$					
$\cdot 329$ 12°	12°		1:4	63 .27	94.28	3 -57	2.15	12192	11494	435	263	13530
				40.43 15.03 10.70	$\begin{array}{c} 73 & 30 \\ 67 & 40 \\ 72 & 91 \end{array}$	$\begin{array}{c} 19 \cdot 90 \\ 22 \cdot 30 \\ 21 \cdot 80 \end{array}$	$\begin{array}{c} 6 & 80 \\ 10 & 30 \\ 5 & 29 \end{array}$					
·325 16°	16°		1;8	91.99	68.14	20.74	7.37	12845	9234	2664	947	(?) 19492
				37.34 10.45	80 •07 80 •07	$16.07 \\ 1.57$	$\begin{array}{c} 3 \cdot 86 \\ 1 \cdot 90 \end{array}$					
·2895 20°	20°		1:8	47 .79	29.88	12.88	3 .45	10465	8756	1348	361	13552
_		Ì	-	-		-		-	_	-		

I. Action of Copper on Nitric Acid-continued.

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97 to 98 per cent. being nitric oxide, the residue in all cases consisting of nitrous oxide and nitrogen. The composition of this residue appears, indeed, to be somewhat variable : but in considering the composition of the residue it is to be remembered that the apparatus cannot be completely exhausted of air before the metal is brought into contact with the acid; that probably there is a slight leakage in of air during the experiment; and that it is difficult to avoid errors in the analysis of the gas remaining after the removal of the nitric oxide, as the quantity which remains is extremely small, even if as much as 10 c.c. be analysed—and more than this was seldom employed, from 5 to 7 c.c. being the quantity usually taken for an analysis. Taking the average of the experiments, we are probably not far wrong in assuming that slightly more nitrous oxide than nitrogen is produced.

Turning now to the experiments with more concentrated and with weaker acid, it will be seen (Experiment II) that, having regard to the composition of the gas produced, the 1:1 acid has about the same action as the weaker 1: 2 acid, but the result obtained with the more concentrated 1:0 acid (Experiment I) is very different, probably in consequence of the retention of the nitrous acid by the nitric acid. The 1: 4 acid (Experiment XI) furnishes a gas containing only about 94 per cent. of nitric oxide, but about twice as rich in nitrous oxide as that furnished by the 1:2 acid. With the 1:8 acid (Experiments XII and XIII), the diminution in the proportion of nitric oxide and increase in the proportion of nitrous oxide and of nitrogen is very marked indeed; so that commencing with the 1:2 acid, it appears that nitrous oxide is produced in an increasing proportion as the strength of the acid diminishes; at the same time the rate at which the copper dissolves also diminishes, but of this we shall say more presently.

The only observations we have instituted as to the influence of temperature have been with the 1:2 acid. Of eight experiments with this acid, six were made by allowing the metal to dissolve in it at the atmospheric temperature; but in the other two (IX and X) the acid was heated to about 50° and 90° respectively before introducing the metal into it, after which the heating was not continued. The metal dissolved much more rapidly in the hot acid, especially in that heated to about 90°; but the gas obtained scarcely differs in composition from that generated on allowing the metal to dissolve at the ordinary temperature.

The volume of gas obtained per unit-weight of metal (63.4 grams) dissolved varies considerably, even in experiments with the same strength of acid: thus, of two experiments with 1:2 acid (IV and VII), the one gave 14928 c.c., and the other only 8584 c.c. This, however, is probably due to the retention of the nitrous acid in solution,

for we have found that the amount of gas obtained by decomposing silver nitrite by nitric acid varies according to the strength of the acid, being greater the weaker the acid. It is always less, however, than is required, on the assumption that the nitrous acid is decomposed in accordance with the equation:

$3\mathrm{HNO}_2 = 2\mathrm{NO} + \mathrm{HNO}_3 + \mathrm{OH}_2.$

For example, in an experiment in which .4493 gram silver nitrite was decomposed by 15 c.c. 1:2 acid, 11,975 c.c. of nitric oxide were obtained instead of 14,880 c.c. required by theory, if 1 litre of hydrogen at 0° and under the pressure of 760 mm. of mercury weigh .089578 gram (Regnault), and 30 grams of nitric oxide are contained by a space of 22.320 litres. We may mention that the decomposition was effected in the glass apparatus shown on p. 59, and that the gas as collected contained 99.25 per cent. nitric oxide; whereas in three similar experiments made at the commencement of the investigation in which the apparatus provided with a caoutchouc stopper was employed, the gas as collected contained nearly two per cent. of nitrogen. That the decomposition of nitrous acid is especially retarded by nitric acid there can be no doubt; for if sulphuric acid be employed, the nitric oxide is given off with greater facility and in larger amount. Indeed, in three experiments which furnished closely accordant results in which silver nitrite was decomposed by a 10 per cent. solution of sulphuric acid, we actually obtained more than the required quantity of nitric oxide, viz., 15800 c.c. The amount of nitric oxide obtained depends, however, very much on the manner in which the experiment is conducted. Gas is at once given off when the acid and nitrite are brought into contact, and a further quantity is evolved as the apparatus is exhausted; but after a time the pump ceases to deliver any appreciable quantity of gas, and in order to decompose any portion of the nitrous acid remaining in solution within a reasonable time, it is necessary alternately to heat the liquid, and then to cool it and pump off the gas in the manner previously described. If weak nitric acid be employed, it is possible by repeating the heating, &c., a sufficient number of times entirely to decompose the nitrous acid in solution, but apparently no amount of heating will effect this if the acid be concentrated; it remains to be investigated whether the nitrous acid is merely held in solution by the nitric acid, or whether it is not actually combined with it-a supposition which cannot be regarded as altogether unwarranted. When copper is dissolved in nitric acid, the gas is evolved in a precisely similar manner, a portion being given off during the dissolution of the metal, a further portion on exhausting, and a very considerable proportion on heating, &c.; but the amount of nitric oxide furnished previous to the application of heat is, as a

rule, less than when silver nitrite is decomposed by nitric acid, and the gas is also given off with much less facility on heating. In fact, the presence of the copper salt appears to exercise a special retarding influence on the decomposition of the nitrous acid, such as no other metal possesses of which we have examined the action on nitric acid. Thus, in the case of zinc, we have found that after the second or third heating the amount of gas evolved is inappreciable, whereas with copper a measureable quantity of gas is often obtained at the eighth or tenth heating. In Experiment VIII, for example, only about onethird of the gas collected was given off in the cold, and the heating had to be ten times repeated before gas ceased to be evolved. It is not improbable, therefore, that in certain cases in which low numbers were obtained (Experiments VII and IX), the heating, &c., was not repeated sufficiently often to entirely decompose the nitrous acid produced during the dissolution of the metal.

If the nitric oxide be, as we have supposed, derived from nitrous acid, the unit-weight of metal should furnish 14880 c.c.; thus:

> $Cu + 2HNO_3 = 2H + Cu(NO_3)_2$ $2H + HNO_3 = HNO_2 + OH_2$. $3HNO_2 = 2NO + HNO_3 + OH_2$ \therefore 3Cu = 2NO or 44.640 litres. and $Cu = \frac{44640}{2}$ or 14880 c.c. NO.

It will be noticed, however, that without taking into account the relatively small quantity of nitric oxide and nitrogen obtained, slightly more than this amount of nitrous oxide appears actually to have been produced in one case (Experiment III); while in three others (Experiments IV, X, and XIV) the nitric and nitrous oxides and nitrogen together are somewhat in excess of the amount which. according to our hypothesis, can be produced. This is probably in the case of Experiments III and IV, at least in part due to the accumulation of a number of positive errors of experiment. In both the gas was collected in five portions; of each of these a portion was analysed, and if the analysis was satisfactory, the remaining portion was merely measured; while if the analysis appeared doubtful, the remaining portion was also analysed, so that the total volume is deduced from ten measurements. Moreover, as in the one experiment '92 and in the other 918 gram of copper was taken, any error in the measurement of the gas is multiplied nearly seventy times in calculating the volume of gas per unit weight of metal; so that a small initial error becomes magnified into a large one. This explanation, however, does not apply to Experiments X and XIV, and for the present we must hesitate to attribute the excess entirely to errors of experiment, especially since, as was above stated, we have also obtained more than the F

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theoretical amount of nitric oxide on decomposing silver nitrite by dilute sulphuric acid; and on this account it is obviously undesirable also to attempt any further explanation until the decomposition of nitrous acid under various conditions has been carefully studied.

One of us has previously shown (J. J. Acworth, this Journal, 1875, p. 830), that when nitric oxide is prepared in the ordinary manner by acting on copper with nitric acid, the gas evolved gradually becomes less pure, and especially richer in nitrous oxide, as the amount of cupric nitrate dissolved in the liquid increases; and it was found that if cupric nitrate were added in the first instance to the acid, the amount of nitrous oxide in the gas produced was very much greater in all stages of the experiment than when the acid alone was employed. But in these experiments relatively large quantities of acid and of copper were used, and portions only of the gas evolved were collected at intervals and analysed. In order therefore, if possible, to ascertain the nature of the influence exerted by cupric nitrate, we have made several experiments in the manner already described, but dissolving nitrate in the acid before bringing the latter in contact with the metal. The results we have obtained are exhibited in Table II.

Apparently the reaction which leads to the production of the nitrous oxide does not take place to any great extent, unless a relatively large amount of the nitrate be present, or the solution be very concentrated. Thus the gas evolved by the action of 1:2 acid, saturated with cupric nitrate (Experiment XVII), contained nearly 10 per cent. of nitrous oxide and a somewhat higher proportion of nitrogen than would have been obtained in the absence of the nitrate; whereas in an experiment (XV) in which acid of the same strength but only 5 grams cupric nitrate were taken, the gas evolved contained about twice as much nitrous oxide as would have been obtained without the addition of the Experiment XVI, in which the conditions were precisely nitrate. similar to those in Experiment XV, furnished a somewhat different result; but the determination of nitrous oxide in this case was unsatisfactory, and we believe that the number given in the table is considerably too low. It should be mentioned that the copper was very much more rapidly dissolved by the saturated solution of cupric nitrate in nitric acid than by the acid alone.

The results of Experiment XIV, compared with those of Experiments III to X show, however, that the quantity of acid employed is of consequence as well as the strength of the acid, about double the proportion of nitrous oxide having been obtained when only 5 c.c instead of the usual amount of 15 c.c. was taken. From this experiment and those with cupric nitrate it may with much probability be concluded that the extent to which the nitrate takes part in the reaction becomes greater in proportion as the amount of nitric acid

			NĽ	TRIC A	CID.					67
c.c. of gas calc. as NO per unit- weight of metal.	Theory = 14880 c.c.		15926		12693 11091		13505			
ht of	$\mathbf{N}_2.$		137		215 320		273			11885
unit-weig tal.	$N_2O.$		482		314 111		1078			348
f gas per mel	NO.		14085		$11140 \\ 9729$		9721			5475
0.1010	Total.		14704		$11649 \\ 10160$		11072			17708
osition	N ₂ .	-74 -55 1 -59	÷6•	2 ·46 ·50	$1.44 \\ 3.15$	$2\cdot40$ $2\cdot49$	2.46	74.47	77 ·27 35 ·90	67 .12
age comp of gas.	$N_2O.$	1 .88 3 ·24 5 ·43	82.8	5 -71	$2.71 \\ 1.09$	11 ·28 8 ·08	74.6	3 ·43	1 -93	1 :96
Percent	NO.	97 ·38 96 ·21 92 ·98	62 · 26	91 ·83 99 ·50	95 -85 95 -76	86 •32 89 •43	87.80	$22 \cdot 10$	$20.80 \\ 64.10 \\ 19.91$	30 ·92
c.c. of gas	obtained.	$52 \cdot 40$ 41 $\cdot 97$ 35 $\cdot 51$	129.88	41 ·26 45 ·56	86 ·82 24 ·36	41 ·74 38 ·42	80.16	43 .77	37.39 26.70	0 00 114 52
Strength of acid	used.		$\left\{\begin{array}{c} 5 \ c.c.\\ 1:2\end{array}\right\}$	1:2 and 5	Erams CuN2O6 ditto	1:2	Sat. WILL CuN2O6		1:2 and	$^{\rm b}_{\rm 4}{ m NH_4}{ m NO_3}$
Ę			11°		13° 12°		10°			13°
Weight of metal	taken.		.092		•4725 •1520		.459			·41
No. of	expr.		XIV		XV XVI		хүп		0	IIIAX

II. Action of Copper on Nitric Acid.

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diminishes, and it may be expected that results of some interest will be obtained by extending the investigation in this direction.

It certainly appeared to be somewhat remarkable, that the presence of an excess of cupric nitrate should lead to an increased production of nitrous oxide, and apparently also, though in a minor degree, of nitrogen. For a long time we were in doubt how to explain its action, until it occurred to us that probably the only way in which it could take part in the reaction would be by undergoing reduction to cuprous nitrate, and that the nitrous oxide was perhaps more or less directly a product of the subsequent re-oxidation of the cuprous nitrate by the nitric acid. This was the more probable as Mr. Acworth had found that the presence of potassium nitrate caused little or no alteration in the composition of the gas evolved from nitric acid and In order to test the validity of our hypothesis, as cuprous copper. nitrate was not procurable, we dissolved cuprous oxide in nitric acid, and the result obtained appears entirely to justify our assumptions. The amount of cuprous oxide taken was 5845 of a gram, and 15 c.c. of 1:2 nitric acid at a temperature of 20° were employed; the oxide dissolved rapidly, and 26-19 c.c. of gas were collected without the application of heat, 11 c.c. being subsequently given off on heating, &c. The percentage composition of the two portions of gas was as follows:

Hence the percentage composition of the total gas (37.19 c.c.) collected is

$$NO = 73.70$$
 $N_2O = 20.38$ $N_2 = 5.92$

and the volume obtained per unit-weight of oxide (142.8 grams)

NO = 6696 c.c. $N_2O = 1852$ c.e. $N_2 = 537$ c.e. Total = 9085 c.c.

The evidence afforded by this experiment as compared with those in which the metal was dissolved in 1:2 acid is of the most definite character, and in our opinion necessitates the conclusion that the hydrogen displaced from nitric acid by copper has less reducing power than cuprous nitrate. It also renders it extremely probable, if it does not actually prove, that the nitrous oxide obtained on dissolving copper in nitric acid of various strengths is not derived from a compound or compounds formed by the reduction of a portion of the acid by the hydrogen displaced from another portion of acid by the metal, but that it is a more or less direct product of the reduction of the acid by the cuprous nitrate; in other words, we incline to the belief that, whatever

the reduction-product or products may be from which the nitrous oxide is directly derived, the hydrogen displaced from nitric acid by copper has not the power of reducing nitric acid to such an extent that nitrous oxide is ultimately produced. But it will be remembered that the amount of nitrous oxide produced increases as the strength of the acid diminishes; hence, if we suppose the reduction to be effected entirely by the hydrogen displaced from the acid by the metal, the hydrogen displaced when the weaker acid is employed would appear to have a greater reducing power than that displaced when the metal is acted upon by the stronger acid, which is obviously contrary to our proposition. Not only, however, is it theoretically improbable that this should be the case, but as we shall show later on when discussing the results of our experiments with other metals, and especially with zinc, where an action similar to that which we have supposed is exerted by the cuprous nitrate is inconceivable, such a conclusion would be entirely opposed, we believe, to the evidence at our disposal. The dissolution of copper takes place, as we have already stated, with increasing slowness as the strength of the acid diminishes; a quantity of metal, for example, which is dissolved by 1:2 acid within 5-6hours requiring 36-48 hours to dissolve in 1:8 acid; and probably this circumstance is the chief, if not the only, cause of the difference in the results observed with acids of different strengths : the explanation which we venture to advance being that a greater number of molecules of cupric nitrate come within the sphere of action of the hydrogen atoms displaced from the acid, and that consequently a greater number of molecules of cuprous nitrate are formed, when the metal slowly dissolves in weak acid than when it more rapidly dissolves in stronger acid. It may be suggested as a more probable hypothesis that the increased production of nitrous oxide is due to the presence of a relatively greater number of molecules of cupric nitrate when weak than when strong acid is used affording opportunity for a greater number of molecules of the former to undergo reduction; our observations (Experiments XV, XVI, and XVII) showing that the amount of nitrous oxide produced on dissolving copper in 1:2 acid in presence of an excess of cupric nitrate, *i.e.*, more than is formed from the metal itself employed in relatively small quantity, is not much increased unless a relatively very large amount of the nitrate be present, would seem, however, to negative such an assumption.

It remains only to consider the evidence afforded by our experiments with copper and nitric acid as to the manner in which the gases evolved are produced. In relation to this question the amount of gas evolved per unit-weight of metal is of especial importance. The amount of nitric oxide theoretically obtainable, supposing this gas to be derived solely from the decomposition of nitrous acid, it will be

remembered is 14880 c.c. per unit-weight of metal; if the nitrous oxide be derived from the decomposition either of nitrosidic acid or of hydroxylamine nitrite (p. 57) the unit-weight of metal should furnish 5580 c.c.; and if the nitrogen result from the action of nitrous acid on ammonia at most 4464 c.c. of this gas could be evolved per unitweight of metal dissolved. The amount of nitric oxide equivalent to the nitrous oxide produced may therefore be calculated by multiplication of the latter by 2.666, and in a similar manner by multiplying the amount of nitrogen evolved per unit-weight of metal by 3:333 we obtain the equivalent amount of nitric oxide. The results of the various experiments thus reduced are exhibited in the last column of Tables I and II. It will be seen that in the majority of cases the amount of gas obtained was below that which can be produced if the nitric and nitrous oxides and nitrogen are formed in the manner we have supposed and the decomposition be complete; and if Experiment XII be excepted, that in those cases in which the theoretical quantity is exceeded (Experiments III, IV, X, and XIV) the excess is comparatively slight. Experiment XII was one of those in which nitrous oxide was largely produced, and the result which it furnished is apparently altogether abnormal, as the amount of gas obtained (19492 c.c.) is nearly one-third in excess of the theoretical quantity. As the result of a second experiment (XIII), under what we believe to have been similar conditions was very different, it might be thought that some error had been committed in the measurement of the gas in the first experiment; but we do not think this probable, especially as the two experiments differ considerably in other respects. Thus it will be observed that in Experiment XII the last portion of gas collected, which consisted almost entirely of that given off on heating, &c., contained a very considerable proportion of nitrous oxide (21.8 per cent.), whereas in Experiment XIII the portion of gas collected in a similar manner contained very little nitrous oxide (1.57 per cent.). In other words, in the one experiment practically the whole of the nitrous oxide was evolved without the application of heat. while in the other a considerable proportion was evolved only on heating. From the observations we have made in the course of our experiments with other metals as to the manner in which nitrous oxide is evolved, we are inclined to believe that that given off in the cold and that given off on heating are products of essentially distinct reactions, and that the former is probably derived chiefly from nitrosidic acid and the latter chiefly from hydroxylamine nitrite. If this be the case, the difference in the results of the two experiments above referred to would appear to indicate that although the conditions seemingly were the same, the reduction had taken place to a greater extent in one than in the other. But this conclusion, interesting as

it is in itself, in no way serves to explain the great "excess" of gas obtained in Experiment XII; in fact it must be admitted that, although the explanation we have advanced holds good in the majority of cases, especially with regard to the manner in which the nitric oxide is formed, there is in others distinct evidence of its insufficiency. It also must not be forgotten that we have determined only the gaseous products, and that, before a complete explanation of the reaction in all its phases can be given, we require, in addition to this, a knowledge of the amount of the reduction-products remaining in solution. The importance of determining these latter will be evident when it is recollected that, as we have already pointed out, a considerable quantity of nitrous acid may escape decomposition into nitric oxide, &c., and is rendered still more obvious by the fact that ammonia may be present in considerable quantity, together with nitrous acid, without much nitrogen being produced, and that therefore the amount of nitrogen obtained-supposing it all to be derived from the decomposition of ammonic nitrate-is but an imperfect measure of the amount of ammonia formed. This is shown to be the case by Experiment XVIII, Table II, where, although 5 grams of ammonium nitrate was added to the 15 c.c. of 1:2 acid in which the copper was dissolved, no less than 30.92 per cent. of the gas obtained consisted of nitric oxide; hence, if it be supposed that an amount of nitrous acid was formed corresponding to the quantity of copper dissolved, less the amount equivalent to the nitrous oxide produced, as much as 39.2 per cent. of the nitrous acid produced underwent the normal decomposition into nitric oxide, &c., notwithstanding the relatively very large amount of ammonium salt present. The amount of nitrogen evolved is within 428 c.c. of that which could be formed from the remaining nitrous acid, supposing that it was completely decomposed in accordance with the equation $HNO_2 + NH_3 = N_2 + 2OH_2$.

§ VI. Action of Silver on Nitric Acid.—The number of experiments we have made with silver is very small, but they appear to us to afford confirmation of the conclusions we have drawn from those with copper. On reference to the following table (III) it will be seen that the gas collected consisted only of nitric oxide and nitrogen: in two of the experiments, however, the amount of nitric oxide obtained was considerably less, and the amount of nitrogen considerably greater, than in the third experiment. This difference in the results is, we believe, due to the fact that in Experiment XIX the gas was pumped off immediately the metal dissolved, whereas in the two other experiments, at least twelve hours elapsed after the metal dissolved before the apparatus was exhausted, in which period a certain amount of the nitric oxide evolved during the dissolution of the metal was

of t.	zht of J taken.	т.	ıgth of used.	f gas ned.	Percer ti	itage co on of ge	mposi- ıs.	c.c. of	f gas per of m	r unit-w etal.	reight
No. exp	Weig meta		Strer	c.c. o obtai	NO.	N ₂ O.	N ₂ .	Total.	NO.	N ₂ O.	N ₂ .
XIX XX XXI	·4 ·4 ·4	$10^{\circ} \\ 11^{\circ} \\ 13^{\circ}$	$egin{array}{c} 1:2\ 1:2\ 1:2\ 1:2 \end{array}$	23 ·17 17 ·78 17 ·30	$98.15 \\ 97.18 \\ 96.70$		1 •85 2 •82 3 •30	$12511 \\ 9601 \\ 9342$	12280 9330 9033		231 271 309

III. Action of Silver on Nitric Acid.

absorbed by the nitric acid and reconverted into nitrous acid: 2NO + $HNO_3 + OH_2 = 3HNO_2$. We may mention that the quantity of silver employed was about four hours in dissolving, and that the dissolution proceeded more and more rapidly as the amount of nitrous acid in solution became greater, which is in accordance with the observations of Russell and others. In Experiment XIX about half the gas was given off previous to heating; while in Experiment XX, of the 17.78 c.c. of gas obtained, 9.5 c.c. were evolved in the cold; and in Experiment XXI, only 5.92 c.c. were collected before heating, and 11.38 c.c. after heating several times. The gas collected after heating in Experiments XX and XXI contained about the same proportion of nitrogen as that collected in a similar manner in Experiment XIX, and as the apparatus employed was that provided with a caoutchouc plug, it is highly probable that the increased amount of nitrogen obtained in Experiments XX and XXI was due to leakage; we are, in fact, almost inclined to regard the whole of the nitrogen obtained in these experiments as derived from external sources, rather than as the product of the action of the silver on the acid, the amount actually collected in Experiment XIX being only '43 c.c., a quantity which is easily accounted for when it is remembered that the exhaustion of the air from the apparatus is necessarily incomplete in the first instance, and that even if actual leakage does not occur at any of the joints, there is undoubtedly a slow diffusion of air through the caoutchouc' plug.

The non-production of nitrous oxide affords strong evidence in favour of the explanation we have advanced of the manner in which this gas is formed when copper is dissolved in nitric acid, for there is no probability in the case of silver that a reaction can take place corresponding to the reduction of cupric to cuprous nitrate; and from its general behaviour, and especially from Thomsen's thermochemical investigations (*J. pr. Chem.* [2], xii, 271), there is every reason to believe that the energy of silver is much below that of copper; consequently if the hydrogen displaced from nitric acid by copper be inca-

pable, as we have suggested, of directly reducing nitric acid to the extent sufficient for the production of nitrous oxide, it is extremely improbable that the hydrogen displaced by silver should have this power, which is in accordance with our observations.

§ VII. Action of Zinc on Nitric Acid.—The results of our experiments with zinc are exhibited in Table IV, from which it will be seen that whatever the strength of the acid, the gas evolved is always a mixture of nitric oxide, nitrous oxide, and nitrogen. As in the experiments with copper, the amount of nitric oxide evolved per unit-weight of metal varies not only with acid of different strengths, but also with acid of the same strength; probably, however, this is at least in part due to the difficulty with which, as we have before pointed out, the nitrous acid produced is entirely decomposed, especially in presence of concentrated nitric acid.

In our opinion the most important element for consideration in the case of the metal under discussion is the amount of nitrous oxide produced, as this probably corresponds strictly with the amount of nitrosidic acid and of hydroxylamine—supposing these to be the two bodies from which the nitrous oxide is more or less directly derived—formed in the reaction: the decomposition of the former into nitrous oxide and water being doubtless immediate, while the production of nitrous oxide by the action of nitrous oxide on the latter, according to V. Meyer's observations (Ann. Chem. Pharm., clxxv, 141), takes place with great facility.

Now it will be observed that the amount of nitrous oxide evolved on dissolving the metal in acid varying in strength from 1:8 to 1:2at the ordinary temperature, that is to say, in Experiments XXII to XXXII inclusive, but excluding Experiment XXIX, is on the whole remarkably constant, the lowest amount being 2422 c.c. (Experiment XXVIII), and the highest 2862 c.c. (Experiment XXII); and as there is no great variation in the amount of nitrogen, these results would appear to indicate that within the specified limits of concentration the extent to which the various reactions take place is influenced in a comparatively slight degree by alterations in the concentration of the From the increased amount of nitrogen produced in Experiacid. ments XXXV and XXXVI, it would almost appear that considerably more ammonia had been produced than in the experiments with This explanation is not a necessary one, however, as weaker acid. another explanation may be given of the increase in the amount of Thus we have already pointed out that the amount of nitronitrogen. gen evolved is but an imperfect measure of the amount of ammonia formed in the reaction, as a considerable proportion of the nitrous acid fails to act on the ammonia present, even if the latter be in great

I													
Per cent. of metal	accounted for	74 ·33 74 ·03	73.64 72.33	70.25	63 .80	$68 \cdot 32$	65 77	89.99		63 .85			68 · 88 70 ·83
ht of	${ m N}_2.$	236 231	$196 \\ 263$	$187 \\ 163$	392	427	244	215		323			330 462
unit-weig tal.	$N_2O.$	2862 2797	2643 2646	2659 2748	2422	2034	2538	2471		2442			$3010 \\ 2271$
f gas per me	NO.	2643 2789	3258 2832	2742 2550:	1730	3320	2304	2454		1914			$1148 \\ 2946$
C.C. 0	Total.	5741 5817	6097 5741	5588 5461	4544	5781	5086	5140		4679			4488 5679
osition	N_2 .	4 ·09 3 ·97	3.24 4.56	3 -32 9 -00	8 .62	7.36	4.80	4.17	$\begin{array}{c} 6 \cdot 31 \\ 9 \cdot 78 \end{array}$	6 · 88	6 59 8 22 7 22	0 . 9 0 8 . 32	7 · 33 8 · 13
age comp of gas.	$N_2O.$	49 ·86 48 ·08	43.35 46.10	47.60	53 · 30	35 ·20	49.90	48.08	60 •17 5 •95	52 ·21	73 -79 73 -79	19 54 19 54	66 - 68 80 - 08
Percent	NO.	46.05 47.95	53.45 49.34	49.08 46.71	38.08	$57 \cdot 44$	45.30	47 . 75	33 ·52 84 ·27	40.91	$22 \cdot 62 \\ 18 \cdot 00 \\ 28 \cdot 61 \\ 18 \cdot 00 \\ 18 \cdot$	52 '2' 72 '14	25.59 51.88
e.c. of gas	obtained.	35 ·33 35 ·33	37 ·52 35 ·33	34.39 34.87	15 -80	$25 \cdot 17$	31.30	31 .63	23 ·73 4 ·06	27 -79	47 ·64 40 ·68	76 ² 52	$\frac{110.48}{19.31}$
Strength of acid	used.	1:8 1:8		1:4	1.4 4.1	1:4	1:2	1:2		1:2			$1:2\\1:2$
Ŀ		0° 2°	ర్ల లో	5°	.9	90°	20	òò		12°			10° 90°
Weight of metal	taken.	¥.7	र्भ र्म्	.4 .415	.226	:283	4	4.		•386			1.6 ·221
No. of	۰٬٩٢	XXII	XXIV	XXVI	XXVIII.	XXIX	XXX	··· IXXX		. пххи			XXIII

IV. Action of Zinc on Nitric Acid.

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o. of	Weight of metal	T.	Strength of acid	c.c. of gas	Percent	tage comp of gas.	osition	6.6.0	f gas per met	unit-weig al.	ht of	Per cent. of metal
	taken.		used.	obtained.	NO.	$N_2O.$	N ₂ .	Total.	NO.	$N_2O.$	N_2 .	accounted for.
<u>.</u>				19.62 2.76	24 ·70 77 ·84	99.99 99.99	8 ·64 13 ·28					
::	•3455 •321	15°	1:1 1:0 1:4 and 5	22 •38 15 •68	31 ·23 ·95	59 -56 78 -29	9 · 21 20 ·76	4210 3175	$\frac{1314}{31}$	2507 2485	389 659	62 ·46 59 ·49
	.4 .242	°,	grams NH ₄ NO ₃ ditto	$41 \cdot 43 \\ 21 \cdot 16$	41 -98 41 -59	37.48 41.25	20 ·54 17 ·16	6732 5928	2826 2466	2523 2445	$\frac{1383}{1017}$	95 •18 83 •16
			sat. sol. MH NO	39 •00 9 • 35	[]	69.8	$\begin{array}{c} 96 \cdot 31 \\ 100 \cdot 00 \end{array}$					
:	641.	12°	100 that	48 .35	1	2 .97	97 •03	17557	I	521	17036	85 · 64

IV. Action of Zinc on Nitric Acid-continued.

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excess; that this is the case is further proved by Experiments XXXVII and XXXVIII, where, notwithstanding 5 grams of ammonium nitrate were added, as much nitric oxide was obtained as in many of the experiments in which no such addition was made. But as the amount of nitrous acid escaping decomposition into nitric oxide, &c., is greater the more concentrated the acid, we may expect that if a greater amount of nitrous acid remain in solution, or, indeed, if it undergo dissociation more slowly when concentrated than when dilute acid is employed, the amount of nitrogen evolved will be greater in the former than in the latter case, even supposing the amount of ammonia present in both cases to be the same.

In Experiments XXIX and XXXIV, in which the acid was heated to about 90° before dropping in the metal, considerably more nitrogen was obtained than in corresponding experiments in which the acid was not thus heated.* A somewhat similar explanation as the above may be advanced in regard to these results, for supposing the same amounts of ammonia and of nitrous acid to be formed under the two sets of conditions, it is probable that more of the ammonia would suffer decomposition by the nitrous acid at the higher temperature.

We are not, however, at all inclined to regard this explanation as sufficient, but believe that our experiments rather justify the conclusion that reduction does take place to a greater extent and proceed further the more concentrated the acid and the higher the temperature. Still this is but a mere opinion, and must remain such until not only the gaseous products, but also those which remain in solution in the acid, shall have been determined.

The last experiment with zinc and nitric acid to which we have to direct attention is that numbered XXXIII, where the amount of metal dissolved was four times as great as in the other experiments under otherwise similar conditions. It will be observed that in this case considerably less nitric oxide and considerably more nitrous oxide was obtained than in any of the experiments with smaller quantities of metal. This probably is due to the fact that when a larger quantity of metal is employed, there is a greater opportunity for the nitrous acid produced by the action of the first portions of metal dissolved to undergo reduction side by side with the nitric acid. It is worthy of note, however, that this "division of labour," so to speak, cannot take place with all metals, for in the case of silver no nitrous oxide is produced, notwithstanding the extreme slowness with which the metal dissolves, and the richness of the solution after a time in nitrous acid.

* Even when cold acid was employed, the metal (very thin foil) dissolved with great rapidity, much heat being developed, so that the mean temperature at which the dissolution of the metal was effected was considerably higher than that of the acid at the commencement of the experiment.

Probably the extent to which nitric and nitrous acids undergo reduction when simultaneously present will be found to be a function of the "energy" of the hydrogen displaced by the action of the metal.

In the Table of Results, on p. 75, an experiment with zinc and ammonium nitrate solution is included which may here be briefly mentioned. Zinc dissolves readily in a concentrated solution of this salt, especially if ammonia be added, much heat being developed; if a moderate amount of metal be taken, and the solution be carefully cooled, no gas is evolved; but on heating the solution a mixture of nitrous oxide and nitrogen is given off, the former increasing in amount with the quantity of metal dissolved. When, after repeated heating, gas is no longer given off, the whole of the nitrite and (?) nitroside appears to have been decomposed, as the solution is immediately coloured by permanganate, even when acidulated, and as the whole of the metal is not accounted for in the form of these gases, it is probable that ammonia is also produced. It is proposed to extend these experiments, and also to observe the action of other metals on ammonium nitrate as well as on other nitrates.

It should here be stated that M. Saint-Claire Deville has published a most valuable account of a number of experiments on the action of zinc on very dilute solutions of nitric acid (solutions containing an amount of acid corresponding to from 2 to 20 grams of the anhydride per litre), and also on mixtures of nitric and hydrochloric acids and of nitric and sulphuric acids (De l'état naissant, *Compt. rend.*, 1870, 1xx, 22, 550). M. Deville, however, appears to regard the various products as formed from the acid by the direct action of the metal, a view which is in opposition to our own. One of us proposes to discuss this subject on a future occasion.

§ VIII. Action of Cadmium and Magnesium on Nitric Acid.—The results of our experiments with these metals are exhibited in Tables V and VI. It will be observed that with cadmium considerably more nitric oxide and less nitrous oxide was obtained than on dissolving zinc in acid of the same strength. There is a considerable difference between the two experiments in the amounts of nitrogen produced, but it will be noticed that less nitrous oxide and more nitric oxide was obtained in that which yielded the larger amount of nitrogen, and it is possible, therefore, that the reduction had proceeded further in this case. The difference may be at least in part due to the fact that a larger amount of the metal was employed in the second experiment.

The behaviour of magnesium as compared with that of cadmium and zinc presents several points of interest. Much less nitric oxide was obtained with this metal than with either of the latter, neither of which, however, furnished so large an amount of nitrous oxide; and

ACW	70RTH	AND	ARM	ISTRO	NG C	N	THE	REDU	OTIC	N OF		
Per cent. of metal	accounted for.		66.86		92 • 30				18.88		26. 06	
ht of	N_2 .		350		163		_		1085		1307	
unit-weig tal.	$N_2O.$		1905		2015				3246		3094	
if gas per me	NO.		8485		7818	_			944		926	
c.c. 0	Total.		10740		9666	-	tric Acid		5275		5327	
osition	\mathbf{N}_2 .	$3.94 \\ 2.11$	3 -26	1 ·85 •60	1.62		m on Ni	$24.41 \\ 14.29 \\ 7.19$	20 .58	26.96 21.40 19.65	24.53	
tage comp of gas.	N_2O .	28.53 1.38	17.74	$\begin{array}{c} 25 & \cdot 88 \\ 2 & \cdot 45 \end{array}$	20.17		Lagnesiu '	$\begin{array}{c} 69.22 \\ 59.31 \\ 12.87 \end{array}$	61 -55	$\begin{array}{c} 62 & \cdot 10 \\ 57 & \cdot 32 \\ 5 & \cdot 70 \end{array}$	58 • 09	
Percen	NO.	12-96 82-29	00.64	72 ·27 96 ·95	78.21	-	tion of A	6.37 26.40 79.94	17.87	$10.94 \\ 21.28 \\ 74.65$	17.38	
e.e. of gas	obtained.	21 ·14 13 ·91	35 .05	$\begin{array}{c} 28 \cdot 13 \\ 9 \cdot 00 \end{array}$	37.13	_	$\nabla I. A_{0}$	47 • 22 13 • 82 6 • 77	18.79	40.52 25 $\cdot34$.3 $\cdot34$	02-69	
Strength of acid	used.		1:2		1:2			1. 20				
E			13°		11°				12°		13°	
Weight of metal	taken.		.3655		•416	_	-		.3085		•314	
No. of	expc.		хы		XLII		_		XLIII		XLIV	

V. Action of Cadmium on Nitric Acid.

the amount of nitrogen produced is far in excess of that obtained with either zinc or cadmium; and there can therefore be little doubt that magnesium is a far more "active" metal than either zinc or cadmium; but the production of so large an amount of nitrogen appears somewhat remarkable, and tends perhaps to throw some doubt on the sufficiency of our explanation of the mode of formation of the nitrogen, as certain of our experiments with zinc (XXXVII and XXXVIII) show that the influence exercised even by a relatively very large quantity of an ammonium salt in increasing the production of nitrogen is by no means great.

As with cadmium, there is a noticeable difference between the amounts of nitrous oxide and nitrogen obtained in the two experiments; and in the case of both metals the lesser quantity of nitrous oxide corresponds with the greater quantity of nitrogen, a lower percentage of metal also being accounted for in the experiments which yield the smaller quantity of nitrogen. This may be in part due to the fact that the heating, &c., was more often repeated in the one case than in the other. There is, however, internal evidence, especially in the case of magnesium, tending to show that this explanation is insufficient; for it will be observed that in the one experiment with this metal the portion of gas last collected-that given off entirely on heating-was far richer in nitrous oxide and poorer in nitrogen than in the other. A similar difference may be observed on comparing the results of two of the experiments with zinc (XXXII and XXXIII). Thus the gas given off on heating contained in the one case only 5.95 per cent. of nitrous oxide, but in the other no less than 19.54 per cent., the only difference between the two experiments being that the amounts of metal taken were not the same (\cdot 386 and $1\cdot$ 6 grams). The results of the two experiments with cadmium also differ in a similar but much less marked manner. If, as we have previously suggested, the decomposition of nitrosidic acid into nitrous oxide and water is immediate, and the nitrous oxide given off on heating is due to the decomposition of hydroxylamine, the differences here referred to indicate apparently that the extent to which the various reactions take place may be considerably affected by what seem to be very slight alterations in the conditions of experiment.

Lastly we may point out as noteworthy that the percentage of metal accounted for in the form of gaseous products is far higher with both cadmium and magnesium than with zinc. It is scarcely possible at present to give any satisfactory explanation of this, especially as zinc would appear to be intermediate in its properties between cadmium and magnesium.

§ IX. Action of Iron on Nitric Acid .- The gases obtained on dis-

No. of	Weight of metal	E	Strength of acid	c.c. of gas	Percent	age compo of gas.	osition	e.e. ot	f gas per 1 met	anit-weigh al.	t of	Per cent. of metal
expt.	taken.		used.	obtained.	NO.	$N_2O.$	N_2 .	Total.	NO.	Ņ20.	${ m N}_2.$	accounted for.
				40 ·79 13 ·43	95 ·77 79 ·29	1.71	$\begin{array}{c} 2 & 52 \\ 20 \cdot 71 \end{array}$			-		
XLV	.251	16°	1:1	54.22	89.16	1.28	7 -04	8064	7392	104	299	64 :23
				35 ·70 20 ·38 7 ·78	83 ·35 97 ·49 90 •74	$\frac{11 \cdot 21}{\cdot 30}$	5 44 2 48 9 26					
XLVI	·3975	13°	1:2	63 • 86	77.88	6 ·26	4.97	2662	5323	375	299	49.18
				$\begin{array}{c} 41 \cdot 33 \\ 6 \cdot 58 \\ 9 \cdot 21 \end{array}$	$\begin{array}{c} 83 \cdot 24 \\ 93 \cdot 76 \\ 94 \cdot 52 \end{array}$	12.17 4.80 1.48	$\begin{array}{c} 4 \cdot 59 \\ 1 \cdot 44 \\ 4 \cdot 00 \end{array}$					
XLVII	.400	10°	1:4	57.12	86.27	62.6	4·14	5330	4598	551	221	45 -72
				$\begin{array}{c} 46 \cdot 98 \\ 8 \cdot 41 \end{array}$	86 ·11 95 ·37	$10.29 \\ 1.98$	$\begin{array}{c} 3 \cdot 60 \\ 2 \cdot 65 \end{array}$					
XLVIII	648.	13°	1:4	55 · 39	87 -50	9.02	3 •48	5456	4773	492	191	45 •15
				34 45 15 85	$\begin{array}{c} 92 \cdot 36 \\ 97 \cdot 15 \end{array}$	4 •58 •99	3 ·06 1 ·86					
XLIX	•318 •200	12°	$\begin{matrix}1:8\\1:12\end{matrix}$	50 •30 30 •81	93 ·87 91 ·28	$\begin{array}{c} 3 \cdot 43 \\ 4 \cdot 45 \end{array}$	2 · 70 4 · 27	5904 5638	5542 5146	202 252	$160 \\ 242$	44 ·44 44 ·51
	_	_			-				-	-		

VII. Action of Iron on Nitric Acid.

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solving this metal* in nitric acid, &c., consist chiefly of nitric oxide, the amounts of nitrous oxide and nitrogen evolved being relatively small. It will be observed, however, that as the concentration of the acid diminishes, the amount of nitrous oxide produced per unit-weight of metal (two-thirds of 56 grams) at first increases and afterwards diminishes; whereas the nitric oxide at first considerably diminishes in amount as the concentration of the acid sinks, but at a certain point increases as the concentration is still further reduced.

These differences in the amounts of nitric and nitrous oxides evolved with different strengths of acid, correspond with perceptible differences in the behaviour of the metal during dissolution. In 1: 1 and 1: 2 acid the iron dissolves very rapidly, producing a pale greenishyellow coloured liquid; in 1: 4 acid, however, it dissolves somewhat less rapidly, and the solution is of a dark brown colour, as also is that produced on dissolving in 1: 8 and 1: 12 acid, which, the latter especially, act upon it still more slowly. From this there can be no doubt that by the action of the more concentrated acid the iron is immediately converted into ferric salt, whereas when weaker acid is employed ferrous salt is first formed, and is converted into ferric salt only on afterwards heating the liquid; and it would appear probable that the hydrogen displaced in the formation of the ferrous salt is more "active" than that displaced in the formation of the ferric salt.

The manner in which the nitrous oxide is evolved appears also to indicate that the hydrogen displaced from weaker solutions of nitric acid is more active in effecting reduction. Thus it will be noticed that in Experiment XLVI, with 1:1 acid, the last portion of gas collected-that evolved on heating-is free from nitrous oxide, which is also the case in Experiment XLVII with 1:2 acid; in this latter experiment; moreover, the second portion of gas collected-that extracted by continuing the action of the pump after practically the whole of the gas evolved during the dissolution of the metal had been removed from the apparatus—is almost free from nitrous oxide. Α second experiment with 1:2 acid, not quoted here, gave precisely similar results. In the case of the weaker acid, however, the gas evolved on heating contains a considerable proportion of nitrous oxide, which, as we have before suggested, is probably derived from the decomposition of hydroxylamine, whilst that immediately evolved without the application of heat is probably in great part, if not entirely, the product of the decomposition of nitrosidic acid.

§ X. Action of Nickel, Cobalt, Indium, and Aluminium on Nitric Acid.

* The iron employed was a portion of the pure iron prepared by the late Dr. Matthiesen, for which we are indebted to Dr. Russell, F.R.S.

+ A mixture of ferrous and ferric salt is doubtless produced with certain strengths of acid, in proportions varying with the concentration of the acid.

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-The results obtained with these metals are represented in Table VIII; although few in number, they appear to us to possess very considerable interest.

Nickel.-This metal would seem to be far more "active" than iron, as it yields a much smaller amount of nitric oxide, and a considerably larger amount of nitrous oxide: the low percentage of metal accounted for is probably to be regarded as evidence of the production of a considerable amount of ammonia, and affords additional proof of the "activity" of nickel. The amounts of nitric and nitrous oxides produced in the two experiments differ considerably, but different amounts of metal were dissolved, and here again it will be noticed that the lesser amount of nitric oxide and the greater amount of nitrous oxide is obtained from the larger amount of metal, which may be accounted for, as we have before said, if we suppose that the nitrous acid produced in the first instance undergoes reduction side by side with the Nickel, at least in the form in which we have employed nitric acid. it.* dissolves with extreme slowness in nitric acid, the time occupied in effecting the dissolution of the quantities taken in Experiments LI and LII having been upwards of 50 and 70 hours respectively.

* I am indebted to Dr. Russell for the nickel and cobalt used in these experiments. They were portions of the pure metals prepared for his researches on the atomic weights of these elements (this Journal, xvi, 51; xxii, 294). The nickel was in the form of hard, dull greyish lumps. On analyzing the gaseous mixture evolved on dissolving it in nitric acid, it was found to contain hydrogen, of which 1.47 c.c. was obtained in Expt. LI, and 2.28 c.c. in Expt. LII, or 625 c.c. and 617 c.c. respectively from 100 grams of nickel. As in the course of this investigation the production of hydrogen has never been observed on dissolving metals in 1:2 acid, or indeed in nitric acid of any strength, and as moreover no hydrogen was obtained on dissolving fused commercial nickel (Expt. LIII), there can be no doubt that the hydrogen had been occluded by the metal during its preparation from the oxide by reduction in hydrogen. This fact that occluded hydrogen is without action on nitric acid is, however, of very considerable interest, as it may be possible by the action of nitric acid to ascertain whether, as has been suggested, a portion of the hydrogen occluded by palladium is combined with the metal. I also propose to apply the method to the study of the gases in meteorites, and it may here be remarked that this discovery of the power of nickel to occlude a very considerable volume of hydrogen explains the occurrence of such large amounts of this gas in meteorites which previously on account of the slight power of occluding hydrogen which iron alone appeared to possess, was somewhat difficult of explanation.

No hydrogen was obtained from the cobalt, although it had also been prepared from the oxide by reduction in hydrogen. But the piece dissolved was the only one in the bottle from which it was taken preserving a metallic appearance : the remainder of the specimen had assumed a brown friable condition, having evidently undergone oxidation. I am inclined to believe from this that the cobalt had originally been charged with hydrogen, with the exception of the piece used by us, which was extremely dense and compact. The spontaneous oxidation of metals prepared by reduction in hydrogen is, in fact, very probably always due to the presence of occluded hydrogen.-H. E. A.

No. of	Weight of metal	E	Strength of acid	c.c. of pas	Percent	age compo of gas.	sition	C.C. 0	f gas per met	unit-weigh al.	t of	Per cent, of metal
expt	taken.		used.	obtained.	NO.	N20.	N ₂ ,	Total.	NO.	N ₂ 0.	N ₂ .	accounted for.
						Nickel.	-		-	-		
	-2355 -3695	$\frac{13}{11}^\circ$	111	13 -76	5 37 2 70 1 86	83 31 87 89 82 35	$11 \cdot 32 \\ 9 \cdot 41 \\ 15 \cdot 79$	1935 2127	104 58	1612 1869	219 200	34 ·52 38 ·36
						Cobalt.						
LIV	-4295	18°	1:2	86-4	14.9	22.64	15 •06	1090	63	863	164	19.55
						Indium.						
ΓV	-265	$ 15^{\circ}$	1:2	29.43	49.06	4.49	4.94	8395	2094	376	416	61 · 13
C					7	llumimu	m.					
SLVI	·141	60-65°	1:1	78.4	0.46	4.	5.9	15290	14831	ł	ł	1
				_								

VIII.

NITRIC ACID.

Cobalt.—This metal, like nickel, dissolves with extreme slowness in 1:2 acid. From the one experiment we have made it would appear to be as much superior in "activity" to the allied metal nickel as this latter is to iron.

Indium.—A small quantity of this metal was kindly presented to us by Dr. Gladstone, F.R.S. It is acted upon with extreme slowness by 1: 2 acid, the time occupied in dissolving the '265 gram employed in the experiment, of which the results are exhibited in Table VIII, having been upwards of 70 hours. It appears to be possessed of considerable "activity," as from the comparatively low percentage of metal accounted for, and the comparatively large amount of nitrogen obtained, it is probable that a considerable amount of ammonia is formed.

Aluminium.—This metal was so slowly acted upon at the ordinary temperature, that we found it necessary to heat the acid to about 60° — 65° , when it dissolved with moderate rapidity. It appears to resemble silver in its action on nitric acid, and most probably it furnishes only nitric oxide.

§ XI. Action of Tin, Lead, and Thallium on Nitric Acid.—The results of our experiments with these three metals are given in Table IX.

Tin.—In the experiments with 1:0 and 1:1 acid, white (?) metastannic acid separated out as the metal dissolved, but in the remaining experiments clear solutions were obtained, from which no separation took place until they were heated, when, however, the liquid became almost semi-solid. It will be observed that not only the nitric oxide, but also the nitrous oxide and nitrogen increase in amount, and then diminish as the concentration of the acid diminishes, and it is probable, therefore, that, as in the case of iron, there is a difference in the "activity" of the hydrogen, according as the product is a stannic or a stannous salt.

Judging from the composition of the gaseous mixture, and the quantities of gas obtained before and after heating, when 1 : 2 acid is employed (Experiment LIX), it appears probable that in the dissolution of the metal to (?) stannous salt, a relatively small amount of nitrous acid, but considerable amounts of nitrosidic acid and ammonia are produced; and that in the conversion of the stannous into stannic salt, which takes place on heating, chiefly those reactions occur which lead to the production of nitrous oxide.

Lead.—The most noticeable feature with regard to the action of this metal on nitric acid is that comparatively large amounts of nitrous oxide and nitrogen are produced, and as a very considerable proportion of the metal is unaccounted for, it is very probable that much ammonia

					NITR	IC ACH	5.						85
	Per cent. of metal	accounted for.		56 -58 73 -03		$81 \cdot 20 \\ 79 \cdot 52 \\ 71 \cdot 76$		94-14		91.44			90.59
	ht of	N ₂ .		423 433		506 470 390		419		487			947
	unit-weig ^j tal.	$N_2O.$		2616 3263		3481 3558 2816		2379		3164			1636
	f gas per me	NO.		34 724		1148 781 106		2939		1423			5963
	C.C. O	Total.		3 073 4420		5136 4710 3312		5737		5074			8546
	osition	N ₂ .		$13.78 \\ 9.80$	$18 \cdot 26 \\ 8 \cdot 30$	9 ·85 9 ·98 11 ·80		08.4	15 ·65 3 ·26	49.6	<i>.</i> .	$\begin{array}{c} 26.42\\ 1.90 \end{array}$	20.11
IX.	tage com of gas.	N20.	Tin.	$85 \cdot 14 \\ 73 \cdot 82$	77 - 35 77 - 17	67 ·78 75 ·55 85 ·02	Lead.	41 .47	81 -90 41 -89	62 .37	Thallium	88 ·66 7 ·72	19.15
	Percen	NO.		1.08 16.38	2 ⁵ 7 25 93	$\begin{array}{c} 22 \cdot 37 \\ 14 \cdot 47 \\ 3 \cdot 27 \end{array}$		51 ·23	2.45 54.85	28.06		34 ·92 90 ·38	84.69
	c.c. of gas	obtained.		$\begin{array}{c} 21 \cdot 54 \\ 31 \cdot 02 \end{array}$	5 •32 29 •85	35 ·17 33 ·09 4 ·66		10.56	5 ·06 4 ·82	88.6		2 : 38 4.04	6.42
	Strength of acid	used.		1:0 1:1		$\begin{array}{c}1\\1\\2\\1\\8\end{array}$		1:2		1:2			1:2
	T.			14°		$\frac{11}{12^{\circ}}$		14°		11°			30°
	Weight of metal	taken.		-4135 -414		•404 •4145 •415		•381		•403			•3065
	No. of	expt.		TVII		LIX		TXII		TXIII			LXIV

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remains in solution. From the composition of the gases collected before and after heating (Experiment LXIII), it would seem that much of the nitrous oxide is derived from the decomposition of hydroxylamine.

Thallium.-Although much more nitric oxide, and considerably less nitrous oxide is furnished by this metal than by lead, the amount of nitrogen produced is much greater; but as the percentage of metal accounted for is high, the results we have obtained do not appear to warrant the conclusion that thallium is a more "active" metal than lead in respect of its action on nitric acid.

§ XII. Action of Alloys on Nitric Acid .- As yet we have only submitted two alloys to examination, viz., brass and gun metal; the results obtained are exhibited in Table X.

	ight of l taken.	т.	agth of used.	of gas ined.	Percer ti	itage co on of ga	mposi- 1s.	e.e. w	of gas eight d	per u of met	nit- al.	cent. of netal inted for.
	Wer		Stren acid	e.e. c obta	NO.	N ₂ O.	N_2 .	Total.	NO.	N ₂ O.	\mathbf{N}_{2} .	Per 1 accou
Brass	·374	15°	1:2	75 ·35	97 ·02	1.64	1.34	12773	12392	210	171	90.74
Lany 10				$21.82 \\ 23.37$	35 ·70 86 ·46	$57.26 \\ 9.23$	$7.04 \\ 4.31$					
Gun metal.	•317	16°	1:2	45 · 19	61 ·93	32.41	5.66	9038	5597	2929	512	101 •57

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$\mathbf{\Lambda}$	

Our object in making these experiments was, if possible, to throw further light on, and to obtain some explanation of, the differences observed in the behaviour of various metals towards nitric acid. Thermochemical investigation has shown that, as a general rule, a considerably greater amount of heat is developed in the formation of the magnesium compounds than in the formation of the corresponding compounds of either zinc or cadmium, and more in the formation of those of zinc than of those of cadmium; and as from the composition of the gases obtained on dissolving these metals in nitric acid it would appear that the first-mentioned is the most, and the last-mentioned the least "active," we are inclined to believe that the extent to which reduction takes place on dissolving a given metal in nitric acid is a function of the energy developed in the reaction, $R'_n + nHNO_3 \pm$ $Aq = nR'NO_3 \pm Aq + nH$, *i.e.*, in the displacement of the hydrogen of the acid by the metal, including that developed subsequently by the

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action of the water present on the salt which is produced. This, however, we regard at present merely as a working hypothesis, for it must not be forgotten that we have not yet sufficient data to enable us to decide absolutely as to which of two related metals is possessed of the greater "activity," inasmuch as only the gaseous products of reduction have been determined; this being the case even with regard to magnesium and zinc, as although less nitric oxide, and considerably larger quantities of nitrous oxide and nitrogen are furnished by magnesium than by zinc, the percentage of metal accounted for in the form of gaseous products is considerably less in the case of the latter. Moreover, in many instances, at least, reaction takes place not only between the metal and nitric acid, but also between the former and the nitrous acid, which is the first product of reduction of the latter; and that this may have an important influence on the final result, and may much complicate the discussion of the phenomena concerned, is evident from the fact that platinum, for example, will dissolve in nitrous, but not in nitric acid, and that silver, if not insoluble in nitric acid, is certainly much more readily dissolved by nitrous acid. It will be remembered also that the amount of metal employed is not always without influence on the result, and that we have suggested that this is a consequence of the accumulation of nitrous acid in the solution.

Roscoe, however, has shown that zinc and cadmium are considerably more "active" than magnesium in reducing the vanadic compounds, a solution of the pentoxide in sulphuric acid being reduced to a salt of the tetroxide by sulphurous acid and hydrogen sulphide; to a salt of the trioxide by magnesium; and to a salt of the dioxide by zinc, cadmium, and sodium amalgam; and it may be said that these observations are in opposition to our conclusions as to the relative "activity" of magnesium, zinc, and cadmium. But the discussion of the phenomena involved in these changes is doubtless also complicated by the occurrence of a series of reactions; so that, in fact, until we are acquainted with the entire series, and are able to deduce the dynamic values corresponding to the several reactions, we must refrain from drawing conclusions as to the reason of the superior activity of zine and cadmium in reducing vanadium pentoxide, and of the superiority of magnesium in reducing nitric acid.

Moreover, if the activity of a given metal depend, as we suppose, on the amount of "available" energy associated with the hydrogen displaced by the metal from the acid, our present knowledge would lead us to expect that the same metal may produce very different results with different acids, for the reason that probably not only are different amounts of heat developed by the mere displacement of the hydrogen in different acids by the same metal, but the compounds formed by

the displacement of the hydrogen of the acid by the metal doubtless enter into reaction with the water present, and in other ways, and probably very different amounts of heat are developed in these reactions by different salts of the same metal. For the same reason we may expect also that alterations in the conditions of experiment, viz., in the degree of concentration of the acid and of the temperature at which the metal is dissolved, will perceptibly influence the result in many cases. The rapidity with which the metal dissolves may also influence the result; there can be little doubt of this in the case of copper, as we have pointed out, and Deville has shown (Compt. rend., lxx, 20, 550) that a relatively much larger amount of nitric acid is required to prevent the evolution of hydrogen when zinc is dissolved in a mixture of nitric and hydrochloric acids than when it is dissolved in a mixture of nitric and sulphuric acids, a result which he attributes in great measure to the fact that the zinc is dissolved more rapidly by the hydrochloric than by the sulphuric acid.

It is well known that in the formation of many alloys from their constituent metals, much heat is developed. From this it follows that the energy of the associated metals must be reduced, and it appeared to us that if our hypothesis above stated were correct, the comparison of the behaviour of a given alloy with that of its constituent metals towards nitric acid should afford evidence of this: that, in fact, reduction of the acid would take place to a less extent on dissolving a given amount of the alloy than on dissolving corresponding amounts of its constituent metals. Only two experiments have as yet been made, one with brass, and the other with gun metal. The brass employed contained 30.2 per cent. zinc, 69.1 per cent. copper, and 7 per cent. lead and tin; the gun metal 10.90 per cent. tin, 88.5 per cent. copper, and a little lead.

It will be seen on reference to the table, that the brass behaves exactly as copper, the percentage of nitrous oxide and nitrogen being no greater than with copper, and the amount of nitric oxide per unitweight of metal (regarded as copper) is as high as was obtained in most of the experiments with copper alone under similar conditions. So far as its behaviour towards nitric acid is concerned, the zine may indeed be said truly to have undergone transmutation into copper, and this result appears to us to afford much support to the hypothesis we have advanced in explanation of the difference in the behaviour of different metals.

The result obtained with gun metal is more difficult of interpretation; it would seem, however, from the large amount of nitrous oxide produced, and the manner in which it is evolved—chiefly in the cold that whilst the "activity" of the tin is reduced by its association with copper, that of the copper on the other hand, is considerably

raised by its association with tin; but whether the gain to the copper is less than the loss to the tin it is impossible to decide from this one experiment.

A most interesting series of observations on the action of acids on alloys of zinc and copper, and of tin and copper, in various proportions, were published some years ago in this Journal by Messrs. Calvert and Johnson (1866, xix, 434), which appear to us further to support our hypothesis. The method they adopted was to determine the loss experienced in a given time by a given surface of the alloy exposed to the action of a given quantity of the acid at a known temperature, and the results obtained in this way indicate that the influence of a metal such as copper, in reducing the "activity" of metals such as zinc and tin, is very considerable. Thus, whereas an alloy of zinc and copper containing 67.26 per cent. of zinc and 32.74 per cent. of copper, lost 2550 grams per square metre of surface, when exposed to the action of nitric acid of sp. gr. 1.10, an alloy containing 50.95 per cent. of zinc and 49.05 per cent. of copper lost only 45 grams per square metre of surface; and the loss experienced by alloys still richer in copper was even less. Again, whereas an alloy of tin and copper, in the proportion corresponding to the formula Sn₅Cu, containing 90.27 per cent. of tin and 9.73 per cent. of copper, lost 1883 grams per square metre when exposed to the action of nitric acid of sp. gr. 1.25, the alloy represented by the formula SnCu, containing 65.02 per cent. of tin and 34.98 per cent. of copper, lost only 183 grams per square metre; alloys containing a larger proportion of copper were found to be somewhat more acted upon, that of the formula SnCu₅ losing 808 grams per square metre.

Although much important information has been gained as to the behaviour of a large number of the metals with nitric acid, the results narrated in the previous pages are chiefly of value as indicating the directions in which the investigation must be continued in order to obtain the requisite data for the complete discussion of the problem under consideration.

In the first place it will be necessary to study the action upon each other in presence of nitric acid of all the possible reduction products nitrous acid, nitrosidic acid, hydroxylamine, ammonia—under conditions as similar as possible to those which obtain when the metals are dissolved in nitric acid. Then the action of metals on nitric acid must be again submitted to examination, and both the gaseous products and those remaining in solution determined; and as very slight variations in the conditions of experiment often appear to exert an appreciable influence on the final result, it will be necessary to determine the two series of products wherever possible in one and the same experiment.

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In the case of those metals which furnish two series of salts, it will be requisite to examine separately the action of the *ous* salts—of the ferrous and stannous salts, for example, as these may behave very differently from the metals themselves. Lastly, a series of experiments on the action of various metals on the same mixture of nitric and hydrochloric or sulphuric acids will doubtless throw much light on the question of the difference in behaviour of the different metals.

I hope very shortly to be able to give an account to the Society of the results obtained in continuation of this investigation.—H. E. A.