LI. — *On the Existence of Nitrous Anhydride in the Gaseous State.*

By G. LUNGE.

THE above question has been several times investigated, and I have myself published a number of papers on this subject.* What induces me to return to it is a communication to this Society by Ramsay and Cundall (this vol., 187—198). These chemists deny the existence of nitrous anhydride, N_2O_3 , in the gaseous state, but they assume it to exist in the blue or green liquid obtained at a low temperature. In discussing this paper (*Abstracts of the Proceedings*, No. 3, p. 23), Armstrong goes even further by saying: "The method adopted by the authors did not suffice to prove the existence of N_2O_3 , even as a liquid, and their results could be equally well interpreted on the assumption that they were dealing with a solution of NO in N_2O_4 ."

I, for my part, have always felt myself compelled to defend the contrary opinion, *i.e.*, that N_2O_3 exists not merely in the liquid state, but also as a vapour or gas. The reasons given for my opinion are recorded in my previous papers, and will be partly mentioned in the present communication also. If Ramsay and Cundall had refuted them, the matter would rest as they left it. But those authors, although they mention my papers, have paid scarcely any attention to them, and even the little they quote of my results is erroneous. The argument upon which I insisted as the principal one, and which as yet has never been refuted, they do not mention at all.

The reason why I lay stress upon recording my dissent from the opinion held by Ramsay and Cundall, that N_2O_3 does not exist in the gaseous state, is that it clashes with the theory of the vitriol-chamber process, which I have been led to adopt as the only one compatible with a large number of ascertained facts. The immense importance of the process of manufacturing sulphuric acid is my apology for continuing this controversy.

Ramsay and Cundall prepare the material they work on by the action of nitric acid on arsenious anhydride. But they seem to be unaware of the previous researches on the influence which the *concentration* of the nitric acid employed exerts on the composition of the nitrogen oxides produced. I have myself shown, by a number of experiments,† what is the composition of the products obtained with

* See especially *Ber.*, 11, 1232; 12, 357; 15, 495; *Dingl. polyt. J.*, 233, 68.

† *Ber.*, 11, 1641. This paper is quoted, amongst others, by Ramsay and Cundall, but no notice is taken of its contents. [Stenhouse and Groves in 1877 (this Jour., 1877, i, 545) called attention to the effect both of the temperature and of the concentration of the acid on the nature of the gases evolved: they recommend nitric acid of sp. gr. 1.30—1.31, and a temperature of 70° as giving the best result.—EDITOR.]

acids of different degrees of concentration. More especially I have shown that, when nitric acid of greater sp. gr. than 1.35 is employed, large quantities of N_2O_3 are produced along with N_2O_4 , whereas acid of sp. gr. 1.5 produces a gas, composed nine-tenths of N_2O_4 and one-tenth of N_2O_3 . I have also shown* that the blue liquid condensed from the purest N_2O_3 , even when rectified several times over, still contains a little N_2O_4 , because N_2O_3 , on vaporisation, is *partially* dissociated, and NO escapes. Ramsay and Candall, notwithstanding this, say (p. 187): "It is commonly believed that the indigo-blue or green liquid produced by the action of arsenious anhydride on nitric acid has the formula N_2O_3 ," thus ignoring my previous researches quoted by themselves. They work with nitric acid of sp. gr. 1.5, sometimes even adding strong sulphuric acid, and employ the product as a starting point for an investigation of the behaviour of the compound N_2O_3 , whilst they might have learned from my research that their substance would not consist of N_2O_3 , but principally of N_2O_4 . This is indeed evident from their own analyses. Their results vary from 28.5 to 30.4 per cent. of nitrogen, whereas N_2O_3 requires 36.84 N, N_2O_4 30.43 N. The products analysed by them had an indigo-green, olive-green, or red colour. Their own analyses would seem to show that they had obtained no N_2O_3 whatever, and looking at these I cannot understand why they found merely sometimes, but not always, the reddish-yellow colour characteristic of N_2O_4 . In a few cases, they subsequently modify the product by passing NO through or over it, but even then they do not get beyond 31.56 per cent. of nitrogen, and even by mixing the vapour with excess of NO, and condensing the product at -20° to -25° , they merely get up to 32.44 per cent. N, thus obtaining, according to their own calculation, a mixture of 31.3 parts N_2O_3 with 68.7 parts N_2O_4 . Experiments made with such material cannot claim any considerable value for deciding the question in point, since I have shown how easy it is to obtain liquids composed almost entirely of N_2O_3 .

Their analytical methods also exhibit too little regard for previous publications. Their first plan consists in placing the substance, sealed in glass bulbs, in stoppered bottles containing very dilute solution of caustic soda, breaking the bulb by shaking the bottle and titrating the uncombined soda with standard acid. They themselves notice that this process is inaccurate, probably on account of NO being formed. But this had been known long ago, and had been pointed out by myself several times;† even when the titration is

* *Dingl. polyt. J.*, **233**, 68. This is a detailed description of my research, to which attention had been drawn in the short summary published in *Ber.*, **12**, 357.

† Especially *Ber.*, **10**, 1076, and *Dingl. polyt. J.*, **228**, 155.

replaced by an actual estimation of the nitrogen present in the alkaline liquid, the source of error just mentioned must remain.

After this they try some other methods, for some time without success. Amongst these they mention estimating the nitrous acid by means of standard potassium permanganate; this they found to be unsatisfactory "on account of the inconvenient and tedious time-reactions which take place." Since they tried this process with "the neutralised solutions of the previous process," *i.e.*, with such in which they themselves believed (and quite rightly!) a loss of NO to have taken place, I cannot conceive how they could expect it to yield accurate results. But apart from this, they seem to ignore that nitrous acid can be perfectly well titrated with potassium permanganate in acid solutions. This process, first proposed by Feldhaus, has been employed for many years by hundreds of chemists, both English and foreign, at all sulphuric acid works, and I showed as early as 1877 that it can be modified so as to combine perfect accuracy with great speed.* Thousands of tests have been made in this way by myself and many other chemists, and it is daily practised in a large number of sulphuric acid works. If Ramsay and Cundall had not employed a solution of caustic soda, but concentrated sulphuric acid, for dissolving their substance, and if they had carried out the titration according to my method, they would have at once obtained the most accurate results which the principle of the process admits of, *i.e.*, not a direct estimation of nitrous acid as such, but that of the quantity of oxygen required for oxidising it up to nitric acid, from which the N_2O_3 can be indirectly calculated. I, for my part, in the numerous researches where I had to estimate nitrous acid along with other nitrogen oxides, have never contented myself with the permanganate method, but I have always combined with it a direct estimation of the nitrogen, thus estimating both N and O. At first I employed Peligot's method with certain modifications, afterwards the method first discovered by Walter Crum, subsequently used by Frankland and Armstrong, and by G. E. Davis, and further developed by myself, on the foundation of testing its accuracy under varying conditions, by the construction of an extremely convenient apparatus, which I have called the Nitrometer.† It is true that Ramsay and

* *Ber.*, 10, 1074. This communication is referred to in my paper (*Ber.*, 11, 1230), quoted by Ramsay and Cundall themselves. My process is also accurately described in my Treatise on the Manufacture of Sulphuric Acid and Alkali, in *Lunge and Hurter's Alkali Makers' Pocket Book*, in *Fresenius' Quantitative Analysis*, 2, 569, and elsewhere.

† *Ber.*, 10, 434. The publications of Campbell, Warington (*Chem. Soc. J.*, 35, 376), and others, subsequent to mine, need not be detailed here. Warington when carrying out his research, was not acquainted with my nitrometer, although

Cundall ultimately adopted the same principle, but they do not mention the work previously done in this respect, and the apparatus they employ would hardly admit of the thorough and long-continued mixture of the mercury and the acid which it is so easy to attain in the nitrometer,* but difficult to attain with a mercury trough, as experienced by Warington. In point of fact, their analytical results are not very concordant; just the substance with which they make their vapour-density experiments, gave results varying between 31.60 and 32.97 per cent. of nitrogen. Since, moreover, they did not control them by estimating the oxygen, which could have been done so easily and quickly by a proper application of the permanganate method, we cannot in any case consider their analyses as having attained the highest possible degree of accuracy, and this must necessarily influence the validity of the inferences drawn from those analyses with respect of the existence of N_2O_3 in the gaseous state.

We shall now see how far Ramsay and Cundall's observations really support their conclusion that N_2O_3 immediately and completely dissociates on passing into the gaseous state, and hence does not exist at all as a gas. They obtain, by the action of arsenious anhydride on the strongest nitric acid, and cooling, liquids of a greenish or red colour, containing practically nothing but N_2O_4 . By acting on these with a large excess of NO , they ultimately get up to a product containing 31.3 parts of N_2O_3 to 68.7 parts of N_2O_4 , but no further. The passage of oxygen into the blue liquid converts it into $NO_2 + N_2O_4$, but so slowly that they think it is doubtful if the reaction takes place with liquid trioxide. The presence or absence of moisture does not appear to influence the combination.

Evidently all this contributes nothing to the main question, which Ramsay and Cundall seek to decide by estimating the vapour-density of the above-mentioned mixture. They do this by introducing glass bulbs filled with the substance into a tube filled with mercury and inverted in a trough, breaking the bulbs within the tube and measuring the volume of the gas formed within the tube, that is over mercury. From a formula given by J. W. Gibbs, they calculate how far the N_2O_4 present in their substance must have dissociated into molecules of NO_2 , what is the theoretical vapour-density of this mixture, and what the density of the original substance on the

described a year before, otherwise he could have avoided the inaccuracies mentioned by him, p. 386.

* If it were necessary to prove that the nitrometer is very well known and very much employed in England, I might quote the paper by A. H. Allen on new applications of this apparatus, in the *Journal of the Society of Chemical Industry*, 1885, p. 178.

assumption that N_2O_3 had been completely dissociated into NO and $\text{NO}_2 + \text{N}_2\text{O}_4$. With this they compare the densities actually found; and although these do not agree very closely with the theoretical figures, but deviate from them by as many as $2\frac{1}{2}$ units out of about 36, they consider it proved that the N_2O_3 prepared by them does not exist in the state of gas—probably because in most cases the densities found are even lower than those calculated according to their theory.

But do their observations really warrant this conclusion? They work with a liquid containing about 31 per cent. of N_2O_3 without submitting it to the best known analytical methods, so that we cannot be certain of its exact composition, on which everything must depend in this case. They observe the vapour-densities by a process not free from objections, viz., over mercury; they mention themselves that Naumann had found mercury to be slowly attacked by N_2O_4 , and that it was at once somewhat tarnished in their own experiments. This they consider not essential, because they observed no contraction after a few hours' standing; but they overlook that, if NO_2 yields oxygen to mercury, and NO is formed, no change of volume will take place; and if N_2O_4 or N_2O_3 yield 2NO under such circumstances, the volume must even be increased, i.e., the vapour-density must be lowered. Thus we do not precisely know what was the real vapour-density of their substance. But even granting, for argument's sake, the correctness of their estimations, the whole method, based upon the change of vapour-densities, is an extremely uncertain one, owing to the presence of nitrogen peroxide. Armstrong, who is altogether disposed in favour of Ramsay and Cundall's view, and even goes beyond them, as we have seen above, still says in discussing the paper, "it was to be hoped that ere long confirmatory evidence that would more directly appeal to chemists would be forthcoming." In other words, even Armstrong implies that those observations, let them be ever so accurate, do not constitute a sufficiently convincing proof of the conclusion based thereon, and other chemists, less favourably predisposed for this conclusion, would probably express themselves more strongly in the same sense. Evidently the whole conclusion falls to the ground, if a little more N_2O_4 was dissociated into 2NO_2 in this case, than Gibbs' formula states for a different condition, viz., for *pure* nitrogen peroxide. But Gibbs' formula cannot lay claim to anything like mathematical accuracy, since the experimental values of the dissociation of N_2O_4 found by the different observers, Playfair and Wanklyn, Sainte-Claire Deville and Troost, Müller, and Naumann, very sensibly differ from one another.

If *everything* were beyond the suspicion of inaccuracy, the analyses of the substance, the method of taking the vapour-densities, Gibbs' formula, its applicability to the case in point, and the coinci-

dence of Ramsay and Cundall's observations with the theory, such extremely indirect argumentation would be convincing; but I consider that I have sufficiently proved that very much indeed is wanting to fulfil these conditions.

The new evidence produced by Ramsay and Cundall in this question is thus seen to be inefficient to solve it. But apart from that, they ought not to have omitted to enter more fully on what had been done before in the same line. Of my labours, pursued through a number of years, and published in a series of communications in the *Berichte* and elsewhere (most of them noticed in the Abstracts of this Journal as well), they say nothing but this: "Lunge has endeavoured to show that the gas absorbed by sulphuric acid consists wholly of N_2O_3 . His argument is that if dissociation were to take place the nitric oxide would escape absorption." Thus they completely pass over that argument which I had pointed out as by far the strongest (to be referred to directly); and what they do quote is perverted into an absurdity, evidently by the above-mentioned neglect of taking into account the concentration of the nitric acid. I, on the contrary, have shown, in opposition to the assertion of others (in several papers which otherwise do not refer to the controversy here treated), that N_2O_4 , which I had proved to be formed from As_2O_3 and strong nitric acid, is completely absorbed by sulphuric acid!

My main argument was as follows:—If N_2O_3 could not exist in the state of gas, but were completely dissociated into a mixture of NO and N_2O_4 (for the sake of simplicity I shall not always add NO_2 , which is evidently unimportant in this case), then, on adding an excess of oxygen to this mixture, all the NO must pass into N_2O_4 , and the analysis must show nothing but N_2O_4 . Opposed to this is the fact (*Ber.*, **11**, 1233) that in the gases escaping from vitriol-chambers, which contain a large excess of oxygen, the nitrogen-compounds in normal working conditions show the empirical formula N_2O_3 , whilst the above theory would lead one to expect N_2O_4 . That the empirical composition of the nitrogen oxides in normal chamber-exit gases is really N_3O_5 , and not N_2O_4 , I have since shown in a much more complete and rigorous way in a research carried out with Naef on the vitriol-chamber process (*Chemische Industrie*, 1884, p. 5). The assumption that the compound present in the vitriol-chambers is not N_2O_3 but NO_2H , is excluded by our experiments with chamber gases, since all suspended liquid substances were retained by a long layer of cotton-wool, and hardly anybody will assume NO_2H to exist in the state of vapour. But apart from this indirect argument, I have experimentally investigated the matter in the winter months 1878–1879. The result has been published in abstract (*Ber.*, **12**, 357), and in detail (*Dingl. polyt. J.*, **233**, 63). I have there proved with cer-

tainty that a gas, evolved from nearly pure liquid N_2O_3 , and carefully analysed, mixed with dry air *never* passes completely into N_2O_4 , even when employing an immense excess of oxygen ($10\frac{1}{2}$ times that required by theory) and working at various temperatures ranging from 4° to 150° . In the presence of 1.7 times as much oxygen as required by theory to convert N_2O_3 into N_2O_4 , as much as 75 per cent. of the N_2O_3 were found to be unchanged, and to have escaped dissociation. As I have minutely described the apparatus and the method of working, and quoted the analytical figures in detail, it would have been easy to criticise or refute any parts of my research that were erroneous. But this has never been attempted from any quarter, and hence my conclusion is not called into question, viz., *that nitrogen trioxide on passing into the state of gas certainly is partly dissociated, but is partly unchanged*. Since, moreover, my experiments plainly show the dissociation of N_2O_3 to increase with an increase in the quantity of air added, and since, on adding such a quantity of air that its oxygen corresponded with 1.7 times that required for oxidising the N_2O_3 to N_2O_4 , still 75 per cent. of N_2O_3 were found to be unchanged, *more than 75 per cent. of N_2O_3 must be left unchanged when simply vapourising without adding any air, and only a comparatively small proportion must be dissociated*. This explains why, on rectifying the blue liquid, no pure N_2O_3 is obtained, a little NO always escaping, but the condensed liquid consists *mostly* of N_2O_3 . The assumption that this N_2O_3 is only formed at the moment of condensation by a combination of NO and N_2O_4 , is rendered very improbable even by Ramsay and Cundall's observation, according to which, *on mixing the vapour of their products with a great excess of nitric oxide and cooling, liquids of at most 31 per cent. N_2O_3 were obtained*. Another observation of those chemists equally supports my results. They found that *liquid nitrogen trioxide is very slowly, if at all, oxidised to N_2O_4 by passing oxygen through it*.* This makes untenable the view held by Armstrong, according to which it was open to assume that Ramsay and Cundall (and, of course, all their predecessors) were dealing with a solution of NO in N_2O_4 . Immediately afterwards, however, Armstrong himself acknowledges this view to be incompatible with the observation that the blue liquid was oxidised with such difficulty, and this must necessarily apply to the gaseous state of N_2O_3 as well, for which I had long ago with all stringency proved a completely analo-

* Hasenbach and Fritsche say that they converted liquid N_2O_4 , containing N_2O_3 , into pure N_2O_4 by passing oxygen through it and rectifying (Michaelis, *Anorgan. Chemie*, 2, 220). But this is perfectly well explained without the oxygen by the rectifying process alone, since N_2O_4 condenses very easily, but N_2O_3 only at a very low temperature (according to my observations not at all above -18°C .), and thus the latter would probably escape, leaving pure N_2O_4 behind.

gous fact. A further argument against the same view is the proof mentioned above, that an excess of NO, brought in contact with liquid or gaseous N_2O_4 , is but slowly and quite incompletely taken up by it to form a substance showing the empirical composition N_2O_3 , whilst it is very easy to prepare the latter directly from As_2O_3 and nitric acid of sp. gr. 1.33.

Hence Armstrong's dictum in the discussion of Ramsay and Cundall's paper: "It was noteworthy that there was no recorded evidence proving the existence of N_2O_3 as gas," is based upon error. Such evidence was produced by me in 1879, and has never been refuted, or even attacked, in any way. That Witt's experiment with aniline (*Ber.*, 12, 1128) does not even touch, and still less refute my main argument, I have proved in *Ber.*, 15, 495; here I shall only say a few words about it. Witt, by passing "Lunge's so-called nitrous anhydride, N_2O_3 ," into a solution of aniline in benzene, obtained diazobenzene nitrate, whilst nitric oxide escaped, and he believed this to prove that the N_2O_3 in the moment of being liberated splits up into N_2O_4 and NO, of which the former alone acts on aniline thus:—

Nitrogen tetroxide he considers, as usual, as the mixed anhydride of nitrous and nitric acid: $NO-O-NO_2$. But there is no difficulty in explaining his reaction by this equation:—

seeing that according to himself (in this respect entirely in concordance with my views) N_2O_4 in contact with sulphuric acid instantaneously yields nitrosyl sulphate and nitric acid, and, on the other hand, NO, acting on a solution of nitric acid in sulphuric acid, immediately furnishes nitrosyl sulphate. All these reactions, as well as the dissociation of N_2O_4 into NO_2 , merely prove how easily the oxygen-atoms combined with nitrogen shift their places; they can no more than mere analyses furnish proof for or against the existence of N_2O_3 in the gaseous state, whilst the facts I have elicited concerning its behaviour towards oxygen can only be explained in the way I have given.