quantitative framework, that is, "it is efficient, representative, accurate and stable". This is typical of most branches of astronomy where there is a hope that improved values will become available and later work will reap the benefit, but there is also the fear that an improvement will change the adopted values and upset work in progress. The analogue of the definitive orbit cannot, however, be used in other branches of astronomy, because values never reach real stability, and in consequence astronomers may set up either a 'rigid' or a 'flexible' system.

In the rigid framework values of all the important constants, as close as possible to the best determinations at the time of adoption, are selected ; but if these values are later found to be in error they are not changed, a correction being applied for those cases that require it, and such a correction can absorb all the effects of improvements in the experimental values. While a rigid framework of this type is necessary for accurate positional astronomy, the one in use at present does not attain perfection ; but the data of its framework are used for the preparation of predictions, and, on comparing these with observational results, discrepancies frequently reflect an inaccuracy in the framework data. Whether such inaccuracies occur or not, the original data remain unaltered so that the process of predicting and observing can continue without interruption, and a clear interpretation can be placed on the observations. This rigid system is not, however, suitable in all cases, and in the more rapidly growing subject of astrophysics, where accuracy is relatively low, a flexible system that caters for perpetual improvement is more appropriate. Here, where the quantitative values vary, the progressive astronomer adjusts his outlook to the knowledge that the values are not precisely known, and he is pleased when the constants fluctuate within the domain of their probable errors. This flexible system shows hope of being available for the whole of astronomy, including astrophysics.

The theme is developed by Prof. Allen; but it is impossible in the limited space to deal with the numerous applications referred to, and this article can do little more than direct attention to the importance of the lecture. Towards the end three conditions, as follows, are mentioned as necessary for building an item into the framework of astronomy : a clear concept and suitable definition of the item ; evidence that the item is vital to the progress of astronomy ; and some estimate of its numerical value. The mean density of the universe is taken as an example on the above basis, although its value is not accurately known. While the density of the visible part made up of stars in external nebulæ is in the neighbourhood of 10^{-29} gm./cm.^{3}, this neglects the possibility of tenuous matter in the inter-nebulæ spaces. For various reasons, including the meagre observational evidence relating to this space, it is pointed out that, if we accept the extreme view of the reddening of the nebulæ as due entirely to gas, the estimate of the mean density of the universe would be increased by a factor of about ten thousand. When the mean density of the universe is open to such doubt, it is realized how far astronomy has still to go. In spite of this doubt, however, the density of the universe has its place in the development of cosmology, and, if it can be placed between the limits 10^{-26}–10^{-30} gm./cm.^{3}, it may possibly be restricted to a narrower range in a few years. "It is already built into the astronomy framework as a quantity to be watched and improved by all means available. If we had no other use for astronomy framework, it would at least be interesting and instructive to see it change as the years go by."

COMPOUNDS OF TERTIARY AMINES WITH NITROSYL CHLORIDE AND WITH DINITROGEN TETROXIDE

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ALIPHATIC and aromatic tertiary amines have been found to react in inert solvents at − 78° with nitrosyl chloride and with dinitrogen tetroxide to yield coloured complexes. The aliphatic complexes are brown and the aromatic plum-coloured. They are insoluble in hydrocarbons but soluble in chlorinated hydrocarbons. The formation of such a complex by trimethylamine and nitrosyl chloride was observed by Jones and Whalen[1], but the generality of this reaction, and its significance in connexion with the reactions of amines with nitrosating agents, have not hitherto been recognized. Amines exhibiting this phenomenon include : trimethylamine, triethylamine, dimethylaniline, diethylaniline, *p*-nitroso-dimethylaniline and N-methyldiphenylamine. The three nitro-dimethylanilines did not form such complexes.

As the complexes are stable only at low temperatures, conventional methods of analysis are inapplicable ; the molecular ratios in which the reactants had combined in two of the complexes were determined as follows. Known quantities of the two reactants were mixed at low temperature in pentane solution, and that in excess was quantitatively removed by pumping under high vacuum into a trap cooled in liquid air, the reaction vessel being maintained at − 78° or − 100°. The excess, collected in the liquid air trap, was then determined. The complexes studied by this means were those of dimethylaniline with nitrosyl chloride in excess, and of dinitrogen tetroxide with trimethylamine in excess. The results are shown in the accompanying tables.

These results establish the formation of $(C_6H_5)(CH_3)_2N.NOCl$ at − 78°, and of $(CH_3)_3N.N_2O_4$ at − 100°.

A good solvent for such complexes is a mixture of *sym.*-tetrachlorethane with ether (70 : 30 by volume). Qualitative observations of the absorption spectra of some of the complexes were made at − 78° in this solvent. Solutions containing an excess of dimethylaniline with nitrosyl chloride and with dinitrogen tetroxide had almost identical absorption maxima. That with nitrosyl chloride appeared at 398 mμ ; and that with dinitrogen tetroxide at 404 mμ.

The electrical conductance of dimethylaniline with nitrosyl chloride was examined in the same solvent

Table 1. DIMETHYLANILINE WITH NITROSYL CHLORIDE
Temp. = −78°
(DMA = dimethylaniline)

Initial ratio NOCl/DMA :	1·53	1·75	1·88	1·92	1·80
Final ratio NOCl/DMA :	1·09	1·06	1·06	1·00	0·91

Table 2. TRIMETHYLAMINE WITH DINITROGEN TETROXIDE
Temp. = −100°

Initial ratio Me_3N/N_2O_4 :	1·5	1·5	1·5	1·9	2·1	2·9
Final ratio Me_3N/N_2O_4 :	0·89	0·98	0·94	1·14	0·92	1·05

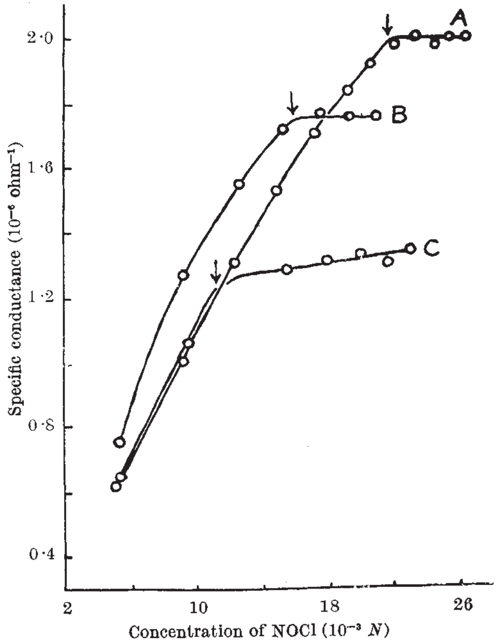

Fig. 1. Normality of dimethylaniline: *A*, 0·0216 *N*; *B*, 0·0158 *N*; *C*, 0·0110 *N*. Equivalence-points marked by arrows

at − 78°. The conductances of a solution of dimethylaniline of constant concentration to which different amounts of nitrosyl chloride had been added are shown in Fig. 1. The conductance rises rapidly with increase of nitrosyl chloride concentration until equimolecular quantities are present, and then remains nearly constant. For comparison, conductance curves for nitrosyl chloride alone, for a tetra-alkylammonium salt, and for dimethylaniline with hydrogen chloride at different concentrations were also obtained under the same conditions, and are shown in Fig. 2. The conductance of the dimethylaniline–nitrosyl chloride complex is of the same order as that of the quaternary ammonium salt, and is much greater than that of dimethylaniline hydrochloride at similar concentrations.

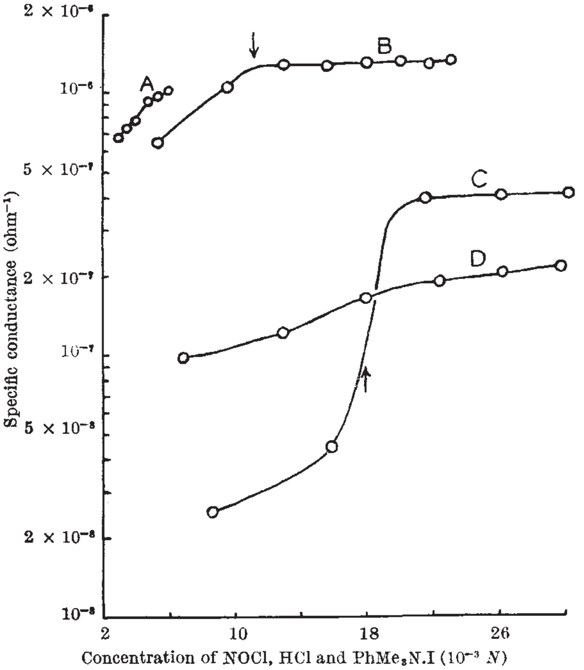

Fig. 2. *A*, Phenyl-trimethylammonium iodide; *B*, dimethylaniline (0·0110 *N*) with nitrosyl chloride (for comparison); *C*, dimethylaniline (0·0179 *N*) with hydrogen chloride; *D*, nitrosyl chloride. Equivalence-points marked by arrows

These results strongly suggest that the complex should be formulated as a nitrosammonium salt:

$$[(C_6H_5)(CH_3)_2\overset{+}{N}.NO]Cl^-;$$

and the similarity of the absorption spectra indicates that the N_2O_4 complex has a similar structure:

$$[(C_6H_5)(CH_3)_2\overset{+}{N}.NO]NO_3^-.$$

The decomposition of the aliphatic complexes is rapid at −55°; the complexes of the aromatic amines are more stable, and their formation can be observed as a transient brown coloration when solutions of the reactants are mixed at room temperature, before the green colour of the nuclear nitroso-compounds appears. The decomposition products of the complex of trimethylamine with nitrosyl chloride were studied in detail by Jones and Whalen[1]; they included trimethylammonium chloride, dimethylammonium chloride, and nitric oxide. Trimethylammonium nitrate and nitric oxide are likewise products of the decomposition of the complex with dinitrogen tetroxide. The decomposition of the dimethylaniline–nitrosyl chloride complex yields *p*-nitrosodimethylaniline hydrochloride: and this is the product isolated when the reactants are brought together at higher temperatures[2].

The decomposition products obtained by Jones and Whalen from their aliphatic complex agree with those assumed by Hughes, Ingold *et al.*[3] in their suggested mechanism for the oxidative dealkylation of tertiary aromatic amines during nitrosation and nitration. The properties of the complexes obtained in the present work correspond closely with those predicted for the intermediate nitrosammonium ion postulated for this dealkylation.

I wish to thank Prof. E. D. Hughes for suggesting this investigation, and Dr. R. Passerini for recording the absorption spectra. [April 14.

[1] Jones and Whalen, *J. Amer. Chem. Soc.*, **47**, 1345 (1925).

[2] Neber and Rauscher, *Annalen*, **550**, 195 (1942).

[3] Glazer, Hughes, Ingold, James, Jones and Roberts, *J. Chem. Soc.*, 2671 (1950).

THE Z-ENZYME IN AMYLOLYSIS

IT has been found by Peat, Pirt and Whelan[1] that crystalline β-amylase is unable to promote hydrolysis of amylose beyond about 70 per cent maltose. Progress is arrested by anomalous linkages, which however can be split by the '*Z*-enzyme', postulated for this purpose, that is present in, for example, soya amylase. Evidence was furnished by Peat, Thomas and Whelan[2] which suggested that the *Z*-enzyme is a β-glucosidase. The exact function of the *Z*-enzyme is clearly a matter of considerable interest and importance.

In experiments performed by us we have confirmed the undoubted existence of the arrest point, and, in general, our soya and crystalline amylases behave like those described by Peat *et al.* However, attempts to identify the *Z*-enzyme with β-glucosidase have been unsuccessful. If potato amylose limit β-dextrin is hydrolysed by soya amylase under conditions favourable to the action of the *Z*-enzyme, we should expect glucose to be liberated first, followed by maltose.