number of wash bottles and attendant laborious manipulations which are needed in the old method, and which constitute yet another drawback to be added to the list given above. Credit for this new device and working out various details in connexion therewith is due to one of my students, Mr. Abdul Basir Pal.

It seems worth while to mention, before concluding, that by working with moist air obtained in this new way and at the same time arranging that the flow of air over the resistance took place at a constant rate, the changes in the resistance due to varying humidities were found by Mr. Pal to be much more regular, reliable, and repeatable than in previous experiments, and thus more helpful and encouraging towards the devising of our electric hygrometer. Full details will be published elsewhere.

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¹ *Proc. Phys. Soc.*, vol. 34, Discussion on Hygrometry.

² *Proc. Phys. Soc.*, vol. 41, p. 29, and *Phil. Mag.*, March 1930, p. 415.

Structure of the Azides, from their Electric Dipole Moments.

As is well known, the chemical evidence regarding the structure of the azides is far from being unambiguous, and four formulæ have been proposed,^{1, 2, 3}

Of these, 2 is ruled out because the central nitrogen atom would have a shared decet of valency electrons, which, for an element in the first short period, is impossible.

Lindemann and Thiele concluded from parachor measurements that the ring structure was the correct one, and it seemed to be of interest to apply other physical measurements to the solution of the problem. Accordingly, the electric dipole moments of phenyl azide, *p*-chlorphenyl azide, and *p*-tolyl azide have been determined and found to be 1.55, 0.35, and 1.96×10^{-18} e.s.u., respectively.

From the comparative smallness of the moment of phenyl azide, formula 3 can be ruled out, as in this the moments due to the C-N link and the N → N link would be at an angle of less than 90° to one another and would probably give a resultant moment of $3-4 \times 10^{-18}$ e.s.u. (compare nitrobenzene $M = 3.9$ and di-phenyl-sulphoxide $M = 4.1 \times 10^{-18}$ e.s.u.). It is possible to discriminate between the two remaining formulæ, because in 1 the negative pole of the group dipole would be farther from the benzene ring than the positive one,⁴ while in 4 the reverse would be the case because of the direction of the co-ordinate link. From the moments of *p*-chlorphenyl azide and *p*-tolyl azide it is clear that actually the negative pole is farther from the benzene ring:⁵

and therefore the ring structure is the most probable of the three. There is, however, a still stronger argument in its favour.

It will be noticed that the moments of *p*-chlorphenyl azide and *p*-tolyl azide are almost exactly equal to the difference and to the sum, respectively, of the

single group moments (the moment 0.35×10^{-18} of the *p*-chlor derivative corresponds to a polarisation of only 2.5 e.c. and by the method of measurement used it is impossible to distinguish this from zero, owing to the possible atom polarisation).⁶ This indicates that the moment of the azide group lies almost exactly along the direction of the valency linking it to the benzene ring. Now, neither formula 3 nor formula 4 could lead to this, since the main moment would be in that part of the group which is inclined at an angle, not equal to 180°, to the C-N link. In the ring formula, however, the moment of the N=N link would be zero, and that of each N-N link, though the nitrogen atoms are not in exactly the same state of combination, would be almost zero. Therefore the only appreciable moment would be that of the C-N link itself, and this would explain the fact observed.

It is therefore fair to say that the evidence of the dipole moments is strongly in favour of the original ring structure.

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¹ Curtius, *Ber.*, 23, 3023; 1890.

² Thiele, *Ber.*, 44, 2524; 1911.

³ Lindemann and Thiele, *Ber.*, 61, 1529; 1928.

⁴ Hammick, New, Sidgwick, and Sutton, *Jour. Chem. Soc.*, p. 1876; 1930.

⁵ J. J. Thomson, *Phil. Mag.*, 46, p. 497; 1923; J. W. Williams, *Physikal. Zeit.*, 29, p. 174 and p. 683; 1928; Hammick, New, Sidgwick, and Sutton, *Jour. Chem. Soc.*, p. 1876; 1930.

⁶ Debye, "Polare Molekeln", Leipzig, 1929, p. 43.

Raman Spectra of Liquid Mixtures.

It is well known that mixtures of polar liquids often exhibit marked deviations from the additive law in respect of such properties as density, vapour pressure, viscosity, and refractive index. Such changes taking place in aqueous solutions are usually attributed to the formation of definite hydrates. Important evidence concerning the constitution of liquid mixtures is furnished by a study of their Raman spectra. I have made a careful examination of the spectra of aqueous solutions of methyl alcohol, acetic acid, and pyridine over a series of concentrations, and have shown that marked variations occur in the spectra. The phenomena noticed include cases in which some Raman lines of the solute suffer displacements, or broaden or split up into components, or undergo changes in relative intensity.

It must suffice here to mention only the effects observed in acetic acid-water mixtures. These refer principally to the behaviour of the broad line of wave-number displacement 1667 found in the spectrum of pure acetic acid and usually attributed to the C=O bond in the molecule. Slight dilution of the acid to 95 per cent strength introduces a new faint component to this line at 1712 cm.⁻¹. The latter is observed to increase in intensity relatively to the first on further dilution to 90 per cent and 85 per cent concentrations. Finally, at 75 per cent, which corresponds nearly to the composition CH₃.COOH, H₂O, only one broad line at 1712 cm.⁻¹ is present. Further dilution produced no change, except for a slight sharpening of the 1712 line.

From these observations, it would appear that a hydrate is formed of the composition mentioned. It may be remarked that the acetic acid solutions exhibit a point of maximum density at about the same concentration (77 per cent) at 25° C.

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