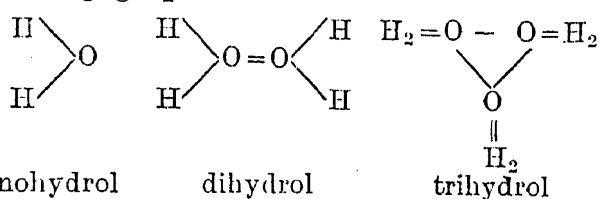


on the basis of these assumptions, the susceptibility of steam at 100°C. is -0.7674×10^{-6} . The experimental results of Auer⁴ show on the other hand that the temperature co-efficient of susceptibility of water is not constant and is itself a function of temperature.⁵ A recalculation of the above values is not possible on account of the insufficiency of Auer's data.

The fact that the values of susceptibility of H_2O , $(H_2O)_2$ and $(H_2O)_3$ should go on diminishing seems to be in itself significant. It has been shown by Ramachandra Rao and Varadachari⁶ that the various hydrates of H_2SO_4 , like $H_2SO_4 \cdot H_2O$, etc., show a decrease in diamagnetic susceptibility as computed from the additive law. Thus if SO_4^{--} ion is substituted by O^{--} ion in H_2SO_4 hydrates, we obtain the water polymers; the decrease in diamagnetic susceptibility resulting from polymerisation in water is seen to be consistent with the observations on the hydrates of sulphuric acid. The percentage deviation from the mixture law is about 10% in $(H_2O)_3$ and about 7% in $(H_2O)_2$; the order of deviation in sulphuric acid hydrates varies from 3 to 4 per cent.

From measurements on the variation of density of water with temperature, Sutherland⁷ has concluded that water consists mainly of $(H_2O)_2$ molecules, whereas $(H_2O)_3$ molecules predominate in ice. He has suggested for these molecular aggregates the following graphic formulæ:



Brühl considers that monohydrol is an unsaturated compound with quadrivalent oxygen. According to the above structural formulæ, it is clear that while the oxygen atom is divalent in monohydrol, it becomes quadrivalent in di- and tri-hydrols.⁸ The change in valency is attended by a

⁴ *Ann. d. Physik*, 1933, **18**, 593-612.

⁵ Auer's values of the temperatures co-efficient of susceptibility (α) at various temperatures ($\theta^\circ C$) can be satisfactorily represented by the empirical formula: $\alpha \times 10^4 = 0.35 + \frac{16.4}{3.43 + \theta}$

⁶ *Curr. Sci.*, 1934, **3**, 250.

⁷ *Phil. Mag.*, 1900, **50**, 460.

⁸ It is assumed by some that the oxygen atom in carbon monoxide is also quadrivalent, i.e., $C \equiv O$.

corresponding change in diamagnetism and we therefore observe that in passing from mono- to di-hydrol the deviation from the additive law is more than 7%. But as we proceed from dihydrol to trihydrol where there is no change of valency, the deviation is less than 3%.

From the values obtained for the mono-, di- and tri-hydrols it is seen that each particular type is by itself diamagnetic. Since diamagnetism shows no variation with temperature and the additive law holds in general for diamagnetic liquid mixtures, we cannot possibly ascribe the temperature variation of susceptibility of water to any other cause except the variation in the relative abundance of the polymers at different temperatures, each polymer being assumed to have a particular value of diamagnetic susceptibility which does not vary with temperature.

I thank Mr. B. Nagesha Rao, Post-graduate student, for checking my calculations.

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Free Phenolic Group in Lignin (Evidence from Action of Chlorine Dioxide on Aromatic and Aliphatic Compounds).

THE behaviour of a few organic compounds with one or more free phenolic OH, towards chlorine dioxide (to give simple aliphatic acids) has been utilised by Schmidt and co-workers¹ as well as by Fuchs and Honsig² as an argument for assuming the presence of a free phenolic OH group in lignin which behaves in a similar way.

The action of ClO_2 on 20 aromatic compounds with free phenolic OH has been tried and it has been found that all of them were readily decomposed. But when the phenolic groups were protected either by methylation or acetylation, the resulting products also reacted with ClO_2 but less readily. Acetylated or methylated lignin behaves similarly. Aliphatic OH in the side-chain is also susceptible to the oxidising action of ClO_2 and the action is less vigorous when it is methylated or acetylated.

¹ *Ber.*, 1925, **58**, 1394.

² *Ber.*, 1926, **59**, 2850.

As lignin contains beyond doubt, more than one methoxy group attached to the benzene ring, it is obvious that the fact that it is acted upon by ClO_2 does not in any way prove the existence of aromatic OH in the molecule.

It has also been observed that the only substituent that makes the benzene compounds stable towards ClO_2 , is the carboxyl; all others are attacked more or less easily. Even toluene and xylenes are oxidised by this reagent. The di-oxymethylene group, however, has been found to be quite resistant towards ClO_2 .

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Fumeless Digestion of Nitrogen.

ESTIMATION of nitrogen is perhaps the most important item of procedure in modern chemical analysis, over a million determinations being annually carried out by those engaged in scientific research alone. The estimations are usually carried out according to one or the other of the several modifications of the Kjeldahl method,¹ and involve prolonged digestion with concentrated sulphuric acid—an operation which is attended by emission of objectionable acid fumes. Some recent workers^{2,3} have suggested that the residue after wet combustion of carbon can be distilled as such for nitrogen, but such a procedure, especially in the case of soils and other biological materials, leads invariably to retention of nitrogen in the digest, and consequently, low and inconsistent estimates being obtained.

A systematic enquiry into the various factors relating to the digestion has shown the following:—(a) the conversion of organic nitrogen into ammonia proceeds more rapidly in presence of small amounts of water combined with an oxidising agent (preferably chromic acid) than with concentrated sulphuric acid alone. In the case of soils, a mixture of sulphuric acid and water in the proportion of 2 to 1 yields the best results, the entire digestion being complete in 30 mins. During digestion, the proportion of acid to water has to be maintained

constant, so it would be necessary to fit the digesting flask with an air- or water-cooled condenser. (b) The digesting mixture requires only a low flame and does not bump, so the long-necked (Kjeldahl) flask generally used for the purpose can be dispensed with. In fact, both the digestion and the distillation can be conducted in the same flask. (c) The minute quantities of nitrogen still retained in the digest can be easily released by addition of small amounts of zinc just prior to distillation with alkali. Metallic aluminium or Devarda's alloy can also be used for the purpose, but their action is a little too vigorous, and causes alkali spray to pass over into the distillate. (d) In the case of materials containing chlorides, it would be necessary to add a small quantity of mercuric or silver sulphate to the digesting mixture, for, otherwise, free chlorine will be formed and nitrogen will be lost in the elementary form. If the substance (*e.g.*, soil) contains nitrate, the latter should first be extracted with water preferably in presence of a suitable flocculant such as calcium sulphate. The residue is digested in the usual way and the digest, together with the extract containing nitrate, distilled with zinc and alkali, in the manner outlined above.

A simple method embodying the above principles has been developed and applied successfully to the estimation of nitrogen in soils. The procedure is also being extended to other biological materials and to nitrogenous substances in general. Attempts are also being made to combine the above method with that for the estimation of carbon⁴ so that both the determinations can be carried out on the same sample.

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The Occurrence of *Choanephora cucurbitarum* (B. & Rav.) Thaxter on *Cassia Tora* Linn.

IN September 1934 our attention was drawn by Prof. B. Sahni to a dead shoot of *Cassia Tora* infected by the white mycelial hyphæ

¹ Kjeldahl, *Z. anal. Chem.*, 1883, 22, 366.

² Anderson and Schutte, *J. Biol. Chem.*, 1924, 61, 57.

³ Brown, *Ind. Eng. Chem.*, 1927, 19, 629.

⁴ Subrahmanyam, Narayanayya and Bhagvat, *J. Indian Inst. Sci.*, 1934, 17A, 197.