If we consider the consequences of this explanation it is seen that for the α- and β-mannose pentaacetates the acetyl group of the second carbon atom has a different position for the α-compound in comparison with the β-derivative, as its CH_3 group is directed by the respective places of the oxygen atoms of the first carbon acetyl group, whereas such a difference does not exist (or is of another nature) for the other discussed monosaccharides. Hence the testing of the principle of optical superposition in the mannose and rhamnose series should be taken up with caution, taking into account these configurational peculiarities.

POLARIMETRY SECTION   D. H. BRAUNS
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RECEIVED APRIL 6, 1931
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THE VARIATION OF ELECTRIC MOMENT WITH TEMPERATURE

Sir:

Because of the uncertainty which has recently arisen in regard to the possible temperature variation of the moments of molecules in which two dipoles may rotate relative to one another, it has seemed of immediate importance to investigate this effect in such molecules. Ethyl acetate, the moment of which should depend, to a considerable extent, upon the position of the moment of the $O-C_2H_5$ bond relative to that of the $C=O$ group, is found to show no significant variation of moment with temperature between -70 and $+30°$ when measured in dilute solution in heptane. The moment of ethylene chloride in solution in heptane is found to increase uniformly from 1.07×10^{-18} at $-70°$ to 1.41×10^{-18} at $+30°$ in satisfactory agreement with the measurements of Meyer [*Z. physik. Chem.*, [B] **8**, 27 (1930)]. In similar fashion the moment of ethylene chlorobromide in heptane solution is found to increase from 0.92×10^{-18} at $-50°$ to 1.19×10^{-18} at $+30°$. This change is in accord with Meyer's idea that the mutual potential energies of the doublets in the two halves of the molecule cause these halves to occupy such positions relative to one another that the moments are partially canceled. The increase in rotational energy with rising temperature tends to overcome this effect of the mutual potential energies and so increase the moment.

Diethyl succinate which was found to have a moment lower than those of the other dicarboxylic acid esters and, apparently, increasing with temperature [Smyth and Walls, THIS JOURNAL, **53**, 527 (1931)], has been measured over a wide range of temperature in solution in kerosene. The moment increases regularly from 2.01×10^{-18} at $0°$ to 2.47×10^{-18} at $180°$, the latter value being practically identical with the moments of the higher members of the series. The tendency of the succinate molecule to bend in such a way that the doublets partially oppose and cancel one

another at the lower temperatures is evidently overcome by the increased vibrational and rotational energy acquired within the molecule as the temperature rises.

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RECEIVED APRIL 8, 1931
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THE ENTROPY OF POLYATOMIC MOLECULES

Sir:

The theoretical entropy of diatomic molecules has been calculated and discussed quite extensively,[1] but so far as I am aware, no one has as yet tackled the problem presented by the polyatomic molecule. I have recently computed the entropies (at $298.1°K.$) of ammonia and of methane and find quite good agreement with the experimental thermochemical values. As such an agreement represents one of the few possibilities of actual check on the conclusions of band spectra as applied to chemistry, I am writing up the calculation in detail for publication, probably in the *Physical Review*.

The same formulas that were used for diatomic molecules[2] are applicable here but a double summation is necessary, corresponding to the two rotational quantum numbers, j and τ, in the symmetrical top type of rotator. When plausible assumptions are made for converting these summations to integrals, the absolute rotational entropy of each symmetry[3] modification (nuclear quartet and doublet forms in the ratio of 1:2, *respectively*, at high temperatures for ammonia and nuclear quintet, triplet and singlet forms in the ratio of 5:27:4, respectively, at high temperatures for methane) may be calculated. From this was subtracted the "zero point" entropy which is the correction term necessary on account of the experimental difficulties of reaching temperatures sufficiently near the absolute zero and in measuring the extremely small heat effects.

Using the moments of inertia of ammonia as given by Badger and Mecke,[4] the total effective entropy of ammonia is 44.0 E. U. and compares very favorably with the value derivable from the data in Lewis and Randall (p. 557), 43.5.

¹ Fowler, *Proc. Roy. Soc.* (London), **A118**, 52 (1928); Giauque and Johnston, THIS JOURNAL, **50**, 3221 (1928); Rodebush, *Proc. Nat. Acad. Sci.*, **15**, 678 (1929); Villars, *ibid.*, **15**, 705 (1929); **16**, 396 (1930); Giauque and Johnston, *Phys. Rev.*, **36**, 1592 (1930); Giauque, THIS JOURNAL, **52**, 4816 (1930); Rodebush, *Phys. Rev.*, **37**, 221 (1931); Giauque, THIS JOURNAL, **53**, 507 (1931); MacGillavry, *Phys. Rev.*, **36**, 1398 (1930).

² Villars, *loc. cit.*, or Giauque, THIS JOURNAL, **52**, 4816 (1930).

³ *Cf.* Hund, *Z. Physik*, **43**, 805 (1927), for NH_3; Elert, *ibid.*, **51**, 6 (1928), for CH_4.

⁴ Badger and Mecke, *Z. physik. Chem.*, **B5**, 333 (1929).