

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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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 molecules² 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 symmetry³ 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); Giaque and Johnston, *THIS JOURNAL*, **50**, 3221 (1928); Rodebush, *Proc. Nat. Acad. Sci.*, **15**, 678 (1929); Villars, *ibid.*, **15**, 705 (1929); **16**, 396 (1930); Giaque and Johnston, *Phys. Rev.*, **36**, 1592 (1930); Giaque, *THIS JOURNAL*, **52**, 4816 (1930); Rodebush, *Phys. Rev.*, **37**, 221 (1931); Giaque, *THIS JOURNAL*, **53**, 507 (1931); MacGillavry, *Phys. Rev.*, **36**, 1398 (1930).

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

³ Cf. Hund, *Z. Physik*, **43**, 805 (1927), for NH₃; Elert, *ibid.*, **51**, 6 (1928), for CH₄.

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

For methane, three values were computed, depending on which line spacing one assumes to be representative of the moment of inertia. They are 44.1, 42.3 and 42.0; for $I = 10.2, 5.66$ and 5.17×10^{-40} . The last corresponds to the spacing most accurately measured (Raman effect)⁵ and, for various reasons, is probably the correct one. In fact, the agreement with the observed entropy⁶ 42.5 may be adduced as additional evidence for the reliability of this choice.

These results indicate that the actual calculation of thermodynamic equilibria⁷ from band spectra data is not to be much longer limited to reactions between molecules having a maximum of two atoms.

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2,4,5-TRIMETHOXYBENZOIC ACID: A DERIVATIVE OF DEHYDRODEGUELIN

Sir:

It has been shown by LaForge and Smith¹ that, through a series of reactions, the rotenone molecule may be ruptured in a manner which yields derric acid, $C_{12}H_{14}O_7$. Derric acid represents the half of the rotenone molecule which contains the methoxyl groups, but as yet the exact nature of the acid is unknown.

Recently three other insecticides of the same type as rotenone, namely, deguelin, tephrosin and toxicarol, have been described.² It has also been shown that structural relationships exist common to the entire molecule of rotenone, deguelin and tephrosin;³ but the fact which is of immediate interest is that the derric acid portion of the molecule is common to all three substances.

It is desired at this time to report in a preliminary way the results of some experiments which clarify to a considerable degree the problem of the derric acid portion of rotenone and allied materials.

Permanganate oxidation of dehydrodeguelin in acetone solution yields two hydroxy acids, one of which contains the two methoxyl groups present in the starting material and thus represents the derric acid portion of the molecule. This acid crystallizes in plates which may be roughly described as rectangular with notched ends and with constrictions in the center of their long axis. It melts at 210° with decomposition and gives an intense blue color with ferric chloride.

⁵ Dickinson, Dillon and Rasetti, *Phys. Rev.*, **34**, 582 (1929).

⁶ Randall and Mohammad, *Ind. Eng. Chem.*, **21**, 1048 (1929).

⁷ Cf. Ludloff, *Z. Physik*, **57**, 227 (1929), for a general discussion of this problem.

¹ LaForge and Smith, *THIS JOURNAL*, **52**, 1091 (1930).

² Clark, *ibid.*, **52**, 2461 (1930); **53**, 313 (1931); **53**, 729 (1931).

³ Clark, *Science*, **73**, 17 (1931); also a paper now being submitted to *THIS JOURNAL* for publication.