NOTES

The Molecular Diameters of Nitrogen Pentoxide.—Eyring and Van Valkenburgh[1] have just published a determination of the viscosity of nitrogen pentoxide; from this viscosity they calculate a molecular diameter of 8.53×10^{-8} cm. I should like to make a few comments on the application of this value to reaction rate calculations. It is common to all modern theories of unimolecular reaction that the rate of production of activated molecules is calculated by assuming that it is equal to the rate at which these activated molecules would enter into collision if they were present at the Maxwell–Boltzmann equilibrium concentration. In this usage a collision is an interaction which leads to a redistribution of internal energy; the diameter which is appropriate to the calculation of the number of such collisions is not the ordinary kinetic theory diameter, though it must be of the same order of magnitude, if grave difficulties are to be avoided. Thus the 8.53×10^{-8} cm. of Eyring and Van Valkenburgh is of no *direct* significance for the theory of the unimolecular decomposition of nitrogen pentoxide.

The statement of Eyring and Van Valkenburgh that recent calculations[2] show that a diameter of 6×10^{-6} cm. must be used to obtain sufficient activations is hardly correct. When these calculations were made, three years ago, they referred to the particular form of theory proposed by Fowler and Rideal.[3] Since that time more satisfactory theories have been proposed, and also considerable new work has been done on the actual measurement of the reaction rate at low pressures.[4] It now appears that the true homogeneous reaction rate falls off to half its high-pressure value at about 0.005 mm. Reference to the calculations made by the writer[5] before these new data were available shows that, on one particular form of theory, they may be accounted for by using a diameter of about 17×10^{-8} cm., which must be considered a permissible value. The details of the theory are so uncertain that one cannot assert the true diameter for collisional deactivation to be greater than that determined by Eyring and Van Valkenburgh; there is, however, no reason why it should not be.

CONTRIBUTION FROM THE
GATES CHEMICAL LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA
LOUIS S. KASSEL[6]

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[1] Eyring and Van Valkenburgh, THIS JOURNAL, **52**, 2619 (1930).

[2] Tolman, Yost and Dickinson, *Proc. Nat. Acad. Sci.*, **13**, 188 (1927); B. Lewis, *Science*, **66**, 331 (1927).

[3] Fowler and Rideal, *Proc. Roy. Soc.* (London), **113A**, 570 (1927).

[4] Ramsperger, Nordberg and Tolman, *Proc. Nat. Acad. Sci.*, **15**, 453 (1929); Ramsperger and Tolman, *ibid.*, **16**, 6 (1930); Schumacher and Sprenger, *ibid.*, **16**, 129 (1930); Hibben, *J. Phys. Chem.*, **24**, 1387 (1930).

[5] Kassel, *ibid.*, **32**, 1065 (1928).

[6] National Research Fellow.