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.

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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).

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Note on Bimolecular Reactions.—In homogeneous bimolecular reactions, integration of the two velocity expressions, $dx/dt = k(a - x)^2$, when the two reacting molecules are alike or of the same initial concentrations, and $dx/dt = k(a - x)(b - x)$, when the reacting molecules are unlike, leads to the following familiar equations

$$k = \frac{1}{ta} \times \frac{x}{(a - x)}, \text{ and} \tag{1}$$

$$k = \frac{1}{t(a - b)} \times \log \frac{b(a - x)}{a(b - x)} \tag{2}$$

where the symbols have their usual significance. It is a physical necessity that expression (2) reduce to (1) if $b = a$. Yet it is obvious that (2) assumes the form 0/0 when $b = a$.

It has been shown in several places[1] that (2) does become equal to (1) under this condition, by expanding the logarithm term in (2) in series and evaluating the resulting expression. However, the methods quoted require a page or more of mathematical simplification to obtain the desired result. On the other hand, making use of the customary way of evaluating 0/0, we have been able to find in a very simple manner the limiting value of the ratio as $b \longrightarrow a$, and from this to show the identity of the two expressions. It proves to be a rather interesting situation, and since it does not appear in any of the ordinary textbooks on the subject, we thought that it might be worth while to pass it on.

From (2)

$$k = \frac{\log b + \log (a - x) - \log a - \log (b - x)}{t(a - b)} = \frac{0}{0}$$

when $b = a$. Now since this would be 0/0 for all finite values of x and t, for our purpose we may treat these as constants and take

$$\lim_{b \longrightarrow a} \frac{f(b)}{F(b)}$$

Treating b as the variable, and differentiating numerator and denominator separately[2] we get[3]

$$\frac{\frac{1}{b} - \frac{1}{b - x}}{-t}$$

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[1] See, for example, Nernst and Schönfliess, "Einführung in die mathematische Behandlung der Naturwissenschaften," Oldenbourg, Munich, 1923, p. 262 *et seq.;* Taylor, "Treatise on Physical Chemistry," D. van Nostrand Company, New York, 1925, p. 869.

[2] See any standard calculus book for explanation of rule to evaluate 0/0, such as Wilson, "Advanced Calculus," Ginn and Co., 1921, p. 61, or Love, "Calculus," The Macmillan Company, 1921, p. 204.

[3] Although b was constant in the original differential equation, we are considering here the special case when $b \longrightarrow a$, that is, variation in b's value.

and on simplifying $= x/tb(b - x)$. This, of course, when $b = a$, becomes $x/ta(a - x)$, which is expression (1).

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THE SKRAUP REACTION WITH CERTAIN AZO COMPOUNDS

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In the course of an investigation of the possible explanation of the reaction mechanism of the formation of *p*-phenanthroline in the Skraup reaction with *p*-aminoresorcin dimethyl ether, *p*-benzene-azo-resorcin dimethyl ether was subjected to the Skraup reaction and the product was found unexpectedly to be also *p*-phenanthroline; the yield in this case was three times as good as in the same reaction with *p*-aminoresorcin dimethyl ether. The formation of *p*-phenanthroline was also established, in the same way, from *p*-benzene-azo-resorcin, whereas from *p*-aminoresorcin, no crystalline matter could be isolated, on working under the same conditions.

From these facts it seemed that in case of the Skraup reaction with rather unstable amines, better results might follow if the corresponding azo compounds were used as reactants, and here I have extended this study to several azo compounds.

Concerning the study of the Skraup reaction with azo compounds, work has been reported by Claus and Stegelitz[1] and later by Lellmann and Lippert.[2] They established the formation of the corresponding ring compounds in this reaction, but the yield in each case was reported to be very poor. In the present investigation the reactions were carried out with the addition of arsenic acid, this being the only difference from the methods of previous investigations.

TABLE I

EFFECT OF ARSENIC ACID IN THE SKRAUP REACTION WITH AZO COMPOUNDS

Reactants	Products	Yield, g.	
		Presence of H_3AsO_4	Absence of H_3AsO_4
Azobenzene, 10 g.	Quinoline picrate	0.5	0.55
	6,6′-Diquinolyl	5.7	1.2
p-Benzene-azo-resorcin	Quinoline	2.0–2.5	1.4
dimethyl ether	*p*-Phenanthroline	1.35–1.5	0.3

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[1] Claus and Stegelitz, *Ber.*, **17**, 2380 (1884).

[2] Lellmann and Lippert, *ibid.*, **24**, 2623 (1891).